PRACTICAL CHEMISTRY.

A COURSE

OF

PRACTICAL CHEMISTRY

ARRANGED FOR THE

USE OF MEDICAL STUDENTS.

BY

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PREFACE

TO

THE FOURTH EDITION.

In this Fourth Edition of a Course of Practical Chemistry, arranged for the use of medical students, several minor improvements, suggested by further experience in teaching, have been effected.

The analytical portion of the work, in so far as regards the description of the methods employed, has been rearranged.

The new system of atomic weights and formulæ has been employed throughout; but it has not been thought necessary to introduce any general changes in the nomenclature.

W. O.

St. Bartholomew's Hospital:
May, 1869.

PREFACE

TO

THE SECOND EDITION.

In preparing a Second Edition of this Course of Practical Chemistry for the press, the first having been for upwards of three years out of print, many additions and alterations have been made, which it is believed will much increase its usefulness as a laboratory guide.

The first chapter, treating of chemical reactions and manipulation, is quite new; the second, relating to general analysis, has been rewritten; and the third and fourth chapters, treating respectively of toxicological and animal chemistry, have been carefully revised. In the second chapters more particularly, full explanations have been given of the tables for the examination of the several groups of bases and acids; so that the paragraphs relating to the individual

members of the groups need scarcely be considered by the learner save for purposes of reference.

To maintain its adaptability to the wants of the medical student, the old scale of atomic weights has been exclusively employed throughout the body of the work. In a short appendix, however, some tables have been set up, in which the new atomic weights are used, with a view to illustrate the superior simplicity and mutual association of the modern unitary over the older dualistic formulæ. The edition of the work is, moreover, illustrated by Mr. Branston with seventy woodcuts of microscopical preparations and chemical apparatus, all of them made expressly from drawings of the actual objects.

W. O.

ST. BARTHOLOMEW'S HOSPITAL:
June, 1865.

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PRACTICAL CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

§ I.—CHEMICAL REACTIONS.

(1.) CHEMISTS are acquainted with about sixty different kinds of matter which have hitherto proved undecomposable, and are consequently termed simple bodies, or elements. These elements unite with one another in certain definite proportions to form an infinite variety of compounds; each particular chemical compound being always constituted of the same elements, combined together in the same proportion. Common salt, for instance, no matter how obtained, or when examined, is always found to consist of sodium and chlorine, united in the ratio of 23 parts by weight of the former element to 35.5 parts by weight of the latter.

The relative quantity of hydrogen which can enter into chemical combination being less than that of any other element, its combining proportion is taken as the standard of comparison or unity. It is found that 1 part by weight of hydrogen unites with 35.5 parts by weight of chlorine to form hydrochloric acid; and further that in very many chemical compounds 1 part of hydrogen may be displaced by 35.5 parts of chlorine to produce chlorine-derivatives of the respective compounds. Again, when hydrochloric acid is treated

with metallic sodium, every 23 parts of sodium is found to expel 1 part of hydrogen and form common salt, by uniting with the 35.5 parts of chlorine previously combined with the 1 part of hydrogen.

The proportion of an element which unites with 1 part by weight of hydrogen, or which displaces 1 part by weight of hydrogen, to unite with 35.5 parts of chlorine, is called its equivalent. Thus 80 is the equivalent of bromide, 23 the equivalent of sodium, and 39 the equivalent of potassium, because 80 parts of bromide, 23 parts of sodium, and 39 parts of potassium are respectively exchangeable for, or equivalent in combination to, 1 part of hydrogen.

(2.) But it is found in many cases that some multiple of the proportion of an element which unites with or displaces 1 part by weight of hydrogen, constitutes the smallest proportion of that element which actually enters into chemical combination. Thus, although 25 parts of arsenic unite with 1 part of hydrogen to form arsenetted hydrogen, and with 35.5 parts of chlorine to form chloride of arsenic, yet it is allowed on all hands that the molecule* of arsenetted hydrogen contains three separable equivalents of hydrogen united with 75 parts of arsenic; and the molecule of chloride of arsenic contains three separable equiva-

* The determination of the molecule of a compound body is based upon very many considerations, physical as well as chemical, which cannot be fully entered into here. The most important of these considerations relate to specific heat, atomic volume, direct combination, analogy, mode of derivation, and, above all, to metamorphoses by substitution. Thus the molecules of marsh gas, ammonia, water, and hydrochloric acid, might each be represented with one equivalent of hydrogen. But the molecule of marsh gas is represented with four equivalents of hydrogen, because in it $\frac{1}{4}$ or $\frac{2}{4}$ or $\frac{3}{4}$ or $\frac{4}{4}$ of the hydrogen can be displaced by substitution at four successive stages. The molecule of ammonia is represented with three equivalents of hydrogen, because in it $\frac{1}{3}$ or $\frac{2}{3}$ or $\frac{3}{3}$ of the hydrogen may be displaced at three successive stages. The molecule of water is represented with two equivalents of hydrogen, because in it $\frac{1}{2}$ or $\frac{2}{2}$ of the hydrogen can be displaced at two successive stages; while the molecule of hydrochloric acid is represented with one equivalent of hydrogen, because in it the hydrogen must be displaced at once or not all.

lents of chlorine united with 75 parts of arsenic; and, in fact, that 75 parts of arsenic constitute the least indivisible proportion of arsenic which ever enters into a combination. The least indivisible proportion of an element which is found to enter into chemical combination is termed its atom, and the number expressing that proportion is called its atomic weight. Hence the atomic weight of an element sometimes coincides with its equivalent weight, as in the case of sodium, and is sometimes a multiple of its equivalent weight, as in the case of arsenic.

The determination of equivalents is a purely experimental question, which, in the majority of instances, has been answered with almost absolute exactitude; but the determination of atomic weights is a question of judgment, to which in many cases very different answers were until lately accorded. Chemists are now agreed, however, as to the atomic weights of all the most important elements, and their agreement extends equally to atomic weights which are multiples of, as to those which are identical with, the equivalents of the respective elements. It is only with regard to a few of the less known elements that any great difference of opinion now exists as to the correlations of their respective equivalents and atomic weights.

(3.) The following tables exhibit lists of the most important elements, with their accepted atomic weights, their symbols or abbreviated names, and the names and symbols of their principal compounds with hydrogen or chlorine. All the hydrides are volatile, and when in the gaseous state occupy the same volume.

Element.			Hydride.	
Atomic weight.	Symbol.	Name.	Symbol	Name.
1	H	Hydrogen	H_2	
19	F	Fluorine	HF	Hydrofluoric acid
35.5	Cl	Chlorine	HCl	Hydrochloric acid
80	Br	Bromine	HBr	Hydrobromic acid
127	I	Iodine	HI	Hydriodic acid
16	O	Oxygen	H_2O	Water
32	S	Sulphur	H_2S	Sulphuretted hydrogen
14	N	Nitrogen	H_3N	Ammonia
31	P	Phosphorus	H_3P	Phosphoretted hydrogen
11	B	Boron	H_3B	Hydride of boron?
12	C	Carbon	H_4C	Marsh-gas
28	Si	Silicon	H_4Si	Silicated hydrogen

Perissad Metal, &c.			Artiad Metal, &c.		
Atomic weight	Name.	Chloride.	Atomic weight.	Name.	Chloride.
18	Ammonium	NH_4Cl	40	Calcium	$Ca\ Cl_2$
1	Hydrogen	H Cl	87.5	Strontium	$Sr\ Cl_2$
7	Lithium	Li Cl	137	Barium	$Ba\ Cl_2$
23	Sodium	Na Cl	24	Magnesium	$Mg\ Cl_2$
39	Potassium	K Cl	65	Zinc	$Zn\ Cl_2$
108	Silver	Ag Cl	112	Cadmium	$Cd\ Cl_2$
200	Mercury	Hg Cl *	200	Mercury	$Hg\ Cl_2$
63.5	Copper	Cu Cl *	63.5	Copper	$Cu\ Cl_2$
27.5	Aluminum	$Al\ Cl_3$*	59	Nickel	$Ni\ Cl_2$
52.5	Chromium	$Cr\ Cl_3$*	59	Cobalt	$Co\ Cl_2$
56	Iron	$Fe\ Cl_3$*	56	Iron	$Fe\ Cl_2$
75	Arsenic	$As\ Cl_3$	55	Manganese	$Mn\ Cl_2$
122	Antimony	$Sb\ Cl_3$	118	Tin	$Sn\ Cl_2$ & $Sn\ Cl_4$
210	Bismuth	$Bi\ Cl_3$			
196	Gold	$Au\ Cl_3$ Au Cl	207	Lead	$Pb\ Cl_2$
			197	Platinum	$Pt\ Cl_2$ & $Pt\ Cl_4$

* It is doubtful whether the molecules and consequent formulæ of some or all of the chlorides corresponding to the formulæ marked with asterisks should not be doubled. The words "perissad" and "artiad" are applied to both metals and non-metals, accordingly as they combine with an odd or even number of atoms of chlorine or hydrogen.

It is observable that the metals mercury, copper, iron, tin, gold, and platinum, form two distinct chlorides, and, as will be afterwards seen, two distinct sets of oxides and salts, corresponding respectively thereto. Several of the other metals also form two chlorides and two sets of salts, but only the chlorides shown in the table, and their corresponding salts, are familiarly known. Cuprous, aurous, and platinous salts, moreover, are for the most part very unstable, and rarely met with save when specially prepared.

(4.) Each symbol, as exemplified in the above tables, represents one combining proportion, or atom of the element. Thus N stands not for nitrogen in general, but for 14 parts by weight of nitrogen as compared with 1 part by weight of hydrogen. Chemical combination is represented by the apposition of symbols; thus KCl signifies a compound of 39 parts of potassium and 35.5 parts of chlorine united to form 74.5 parts of chloride of potassium. A small figure placed to the right of a symbol indicates a multiple quantity of that particular element. Thus $HgCl_2$, or corrosive sublimate, signifies a compound of one atom of mercury with two atoms of chlorine. A larger figure placed to the left of an allocation of symbols multiplies the entire compound. Thus $3HNO_3$ represents three proportions of nitric acid, a compound body consisting of one atom of hydrogen, one atom of nitrogen, and three atoms of oxygen. The single formula of a compound body represents the atom, or smallest individual proportion, of that particular compound, and its atomic weight is the sum of the atomic weights of its constituents. Thus the atomic weight of nitric acid $HNO_3 = 1 + 14 + 16 \times 3 = 63$.

In writing the formulæ of compound bodies, it is sometimes found advisable to break them up in different ways—by means of periods, brackets, parentheses, &c. Thus for sulphuric acid we sometimes write $H_2O.SO_3$ instead of H_2SO_4; for nitrate of am-

monium, NH_4NO_3 instead of $N_2H_4O_3$; and for phosphate of calcium $Ca_3(PO_4)_2$ instead of $Ca_3P_2O_8$. Sometimes these breaks are purely arbitrary or conventional, and should then be dispensed with as much as possible. At other times they indicate a real molecular isolation of one portion of a compound from the remainder, when their use is perfectly legitimate.

The symbol for the atom of an element is sometimes marked with one or more dashes, to indicate its equivalency or interchangeable value for hydrogen. For instance, Ag is sometimes marked with a single dash to show that the atom of silver may be substituted for an atom of hydrogen, so as to combine with an atom of chlorine, thus $Ag'Cl$. Again, Pb is marked with two dashes, and Bi with three dashes to indicate that the atoms of lead and bismuth may be respectively substituted for two and three atoms of hydrogen, so as to combine with two and three atoms of chlorine, thus $Pb''Cl_2$ and $Bi'''Cl_3$.

The signs +, —, and = are used almost in their ordinary algebraical sense. The sign + signifies addition to, or rather mixture with; the sign — subtraction from; and the sign = equivalency with, or rather conversion into. Thus the equation $2HCl + CuO = CuCl_2 + H_2O$, implies that an atom of hydrochloric acid, mixed with an atom of oxide of copper, yields an atom of chloride of copper together with an atom of water. Or the equation may of course be written $2HCl + CuO - H_2O = CuCl_2$. In modern chemistry the sign + is no longer used to express combination.

(5.) Those hydrogenized compounds which can readily exchange some or all of their hydrogen for its equivalent of metal constitute the acids. From habit one particular reaction is adopted as the conventional criterion of acidity, namely that effected by the hydrates of potassium and sodium. An acid is simply a hydrogenized body which, when treated with hydrate of potassium, can exchange hydrogen

for potassium with simultaneous formation of water, thus :—

$$H_4C_2O_2 + KHO = KH_3C_2O_2 + H_2O.$$

The solutions of such bodies are generally found to have the power of reddening blue litmus paper, and of effervescing with alkaline carbonates, so that the possession of these properties may be looked upon as more or less characteristic of an acid. Oxygenized acids, such as the nitric HNO_3, and acetic $H_4C_2O_2$, are also called ternary, while non-oxygenized acids, such as the hydrochloric HCl, and sulphydric, H_2S, are called binary. These binary acids were formerly known as hydracids. In most ternary acids the number of oxygen atoms is two, or three, or four, as shown below :—

$H\,Cl\,O_2$ Chlorous.	$H\,Cl\,O_3$ Chloric.	$H\,Cl\,O_4$ Perchloric.
$H\,N\,O_2$ Nitrous.	$H\,N\,O_3$ Nitric.	$H\,I\,O_4$ Periodic.
$H\,B\,O_2$ Boracic.	$H_2S\,O_3$ Sulphurous.	$H_2S\,O_4$ Sulphuric.
$H_4C_2O_2$ Acetic.	$H_2C\,O_3$ Carbonic.	$H_2C_2\,O_4$ Oxalic.
$H_3P\,O_2$ Hypophos.	$H_3P\,O_3$ Phosphorous.	$H_3\,P\,O_4$ Phosphoric.

It is not uncommon to have one or more of the hydrogen atoms of a ternary acid which are not replaceable by metal exchanged for chlorine, and some or all of its oxygen atoms exchanged for sulphur. Thus we have acetic acid $H_4C_2O_2$, chloracetic acid $HCl_3C_2O_2$, and sulphacetic acid $H_4C_2S_2$; with their corresponding salts, $NaH_3C_2O_2$ acetate, $NaCl_3C_2O_2$ chloracetate, and $NaH_3C_2S_2$ sulphacetate of sodium, for instance.

(6.) Acids in which only one atom of hydrogen can be replaced by metal are called monobasic. The principal monobasic acids with which the student will have to deal are the following :—

$H\,Cl$	Hydrochloric.	$Na\,Cl$	Chloride of sodium.
$H\,Cl\,O_3$	Chloric.	$Na\,Cl\,O_3$	Chlorate of sodium.
$H\,Br$	Hydrobromic.	$Na\,Br$	Bromide of sodium.
$H\,I$	Hydro-iodic.	$Na\,I$	Iodide of sodium.
$H\,N\,O_3$	Nitric.	$Na\,N\,O_3$	Nitrate of sodium.
$H\,B\,O_2$	Boracic*	$Na\,B\,O_2$	Borate of sodium.
$H_4C_2O_2$	Acetic.	$NaH_3C_2O_2$	Acetate of sodium.

* Another variety of boracic acid has the formala H_3BO_3, and is tribasic.

Acids in which two atoms of hydrogen can be replaced by metal are called dibasic. The most important of them are comprised in the following table:—

H_2O	Hydric acid .	KHO	Potash.
		K_2O	Oxide of potassium.
H_2S	Sulphydric acid	$NaHS$	Sulphydrate of sodium.
		Na_2S	Sulphide of sodium.
H_2SO_3	Sulphurous acid	$NaHSO_3$	Acid sulphite of sodium.
		Na_2SO_3	Sulphite of sodium.
H_2SO_4	Sulphuric acid .	$KHSO_4$	Acid sulphate of K.
		K_2SO_4	Sulphate of potassium.
H_2SiO_3	Silicic acid . .	K_2SiO_3	Silicate of potassium.
H_2CO_3	Carbonic acid .	$KHCO_3$	Acid carbonate of K.
		K_2CO_3	Carbonate of potassium.
$H_2C_2O_4$	Oxalic acid .	KHC_2O_4	Acid oxalate of K.
		$K_2C_2O_4$	Oxalate of potassium.
$H_6C_4O_6$	Tartaric acid .	$KH_5C_4O_6$	Cream of tartar.
		$KNaH_4C_4O_6$	Rochelle salt.

Until lately many of these acids were considered as monobasic and represented by the halves of the formulæ here given; but the evidence of their dibasicity is at present indisputable. This class of bodies includes sulphydric acid, or sulphuretted hydrogen, the sulphur analogue of water, which itself often plays the part of an acid, and is included in the foregoing list.

Acids in which three atoms of hydrogen may be replaced by metal are called tribasic, the most important of which are—

H_3PO_4	Phosphoric acid .	KH_2PO_4	Phosphate of potassium.
		Na_2HPO_4	Phosphate of sodium.
		Ag_3PO_4	Phosphate of silver.
H_3AsO_4	Arsenic Acid .	Ag_3AsO_4	Arseniate of silver.
$H_8C_6O_7$	Citric acid . .	$Ag_3H_5C_6O_7$	Citrate of silver.

Monometallic and dimetallic arseniates and citrates are also familiarly known.

The monometallic salts of dibasic and tribasic acids closely resemble the acids themselves in their action on blue litmus paper and on alkaline hydrates and carbonates. They constitute, indeed, a mere variety of the class of acids.

In polyhydrogenized acids, it does not follow that the units of basicity are equal to the units of hydrogen—acetic acid $H_4C_2O_2$, tartaric acid $H_6C_4O_6$, and citric acid $H_8C_6O_7$ for example, being but monobasic, dibasic, and tribasic respectively, or capable of exchanging respectively but one, two, and three atoms of hydrogen for metal.

(7.) In the illustrative salts above adduced, each atom of hydrogen in the acid has been displaced by one atom of uniquivalent metal. Thus we had nitrate of potassium KNO_3, derived from nitric acid HNO_3; oxalate of sodium $Na_2C_2O_4$, derived from oxalic acid $H_2C_2O_4$; phosphate of silver Ag_3PO_4, derived from phosphoric acid H_3PO_4, &c. &c. But the salts of multiquivalent metals have usually, though not invariably, a somewhat greater complexity of constitution. Their chlorides, derived from two or three atoms of hydrochloric acid, are given on page 16, and their other salts derived from monobasic acids are found to correspond closely with their chlorides. Thus dichloride and dinitrate of tin, $Sn''Cl_2$ and $Sn''(NO_3)_2$, are derived from two molecules of hydrochloric and nitric acid, H_2Cl_2 and $H_2(NO_3)_2$, respectively; trichloride and trinitrate of bismuth, $Bi'''Cl_3$ and $Bi'''(NO_3)_3$, derived from three molecules of hydrochloric and nitric acid, H_3Cl_3 and $H_3(NO_3)_3$ respectively. But the formulæ of the salts of dibasic acids with diquivalent metals and of tribasic acids with triquivalent metals are very simple. Thus lead sulphate $Pb''SO_4$, is derived from sulphuric acid H_2SO_4, and bismuth phosphate $Bi'''PO_4$, from phosphoric acid H_3PO_4, &c. On the other hand, the salts of dibasic acids with triquivalent metals, and of tribasic acids with diquivalent metals, are highly complex. Sulphate of bismuth, for example, must be represented by the formula $Bi'''_2(SO_4)_3$, derived from three atoms of sulphuric acid $H_6(SO_4)_3$, and so in other instances.

(8.) It will be perceived from the above tables and examples that a salt is usually derived from its corresponding acid by a substitution of metal for hydrogen.

Many salts, however, known as salts of the alkaloids, are formed in a different way—namely, by a direct union of the acid with ammonia or some other alkaloidal base; as exemplified by hydrochloride of ammonia NH_3HCl, nitrate of ammonia NH_3HNO_3, &c. But salts of this character may also be considered to contain a composite metal, or rather metalloid, in place of the hydrogen of the acid. Thus by associating with each atom of ammonia in the salt an atom of hydrogen from the acid, each such atom of ammonia NH_3 becomes converted into an atom of ammonium NH_4, a pseudo-metallic grouping, which in its combinations presents a most marked analogy to potassium, as illustrated below:—

Ammonia salts.		Ammonium salts.		Potassium salts.	
NH_3HCl	Hydrochlor.	NH_4Cl	Chloride.	KCl	Chloride.
NH_3HNO_3	Nitrate.	NH_4NO_3	Nitrate.	KNO_3	Nitrate.
$NH_3H_2SO_4$	Acid sulph.	NH_4HSO_4	Acid sulph.	$KHSO_4$	Acid sulph.
$(NH_3)_2H_2SO_4$	Sulphate.	$(NH_4)_2SO_4$	Sulphate.	K_2SO_4	Sulphate.

Without assuming any knowledge of the actual molecular arrangement of ammoniacal salts, it is found most convenient in practice, especially when comparing them with metallic salts, to regard them as salts of ammonium rather than as salts of ammonia. But the salts of the correlated alkaloids aniline, morphia, strychnia, &c., are usually represented after the manner of ammonia salts, thus:—

Hydrochlorides.		Acetates.	
$NH_3 \cdot HCl$	Ammonia.	$NH_3 \cdot H_4C_2O_2$	Ammonia.
$C_6H_7N \cdot HCl$	Aniline.	$C_6H_7N \cdot H_4C_2O_2$	Aniline.
$C_{17}H_{19}NO_3 \cdot HCl$	Morphia.	$C_{17}H_{19}NO_3 \cdot H_4C_2O_2$	Morphia.
$C_{21}H_{22}N_2O_2 \cdot HCl$	Strychnia.	$C_{21}H_{22}N_2O_2 \cdot H_4C_2O_2$	Strychnia.

(9.) It was formerly the custom to regard ternary acids as compounds of one or more equivalents of water with a special oxidized grouping, and the corresponding salts as compounds of one or more equivalents of metallic oxide with the same oxidized grouping. Thus the formulæ of chloric acid and chlorate of potassium were written $H_2O.Cl_2O_5$ and $K_2O.Cl_2O_5$, corresponding to $2HClO_3$ and $2KClO_3$ respectively.

But this custom, which was based on assumptions since shown to be erroneous, is now falling gradually into disuse. Thus the acids of chlorine form the following series, the ternary members of which may be obtained by direct and successive oxidation of the binary member, hydrochloric acid, the hydrogen of which cannot possibly exist in the state of water:—

HCl	Hydrochloric.	KCl	Chloride.
$HClO$	Hypochlorous.	$KClO$	Hypochlorite.
$HClO_2$	Chlorous.	$KClO_2$	Chlorite.
$HClO_3$	Chloric.	$KClO_3$	Chlorate.
$HClO_4$	Perchloric.	$KClO_4$	Perchlorate.

It is true that many ternary acids and salts may be directly or indirectly formed from, or separated into, a special oxidized grouping and water or metallic oxide, but the same acids and salts may also be formed from, or separated into, a variety of other sub-compounds, and the one mode of composition or decomposition has no more right than has each of the others to set up for itself a rational formula. Thus if we act upon sulphate of copper by metallic iron, magnesia, peroxide of barium, and sulphide of sodium respectively, we have the following reactions:—

$$CuSO_4 \text{ or } Cu.SO_4 + Fe = FeSO_4 \text{ or } Fe.SO_4 + Cu$$
$$CuSO_4 \text{ or } CuO.SO_3 + MgO = MgSO_4 \text{ or } MgO.SO_3 + CuO$$
$$CuSO_4 \text{ or } CuO_2.SO_2 + BaO_2 = BaSO_4 \text{ or } BaO_2.SO_2 + CuO_2$$
$$CuSO_4 \text{ or } CuS.O_4 + Na_2S = Na_2SO_4 \text{ or } Na_2S.O_4 + CuS$$

From each of these reactions there might, with equal reason, be inferred the pre-existence in sulphate of copper of the respective groupings SO_4, SO_3, SO_2, and CuS; and the correctness of the respective rational formulæ $Cu.SO_4$, $CuO.SO_3$, $CuO_2.SO_2$, and $CuS.O_4$, in accordance with the theories of Dulong, Berzelius, Longchamps, and Laurent respectively. Moreover, sulphate of copper may be electrolyzed into Cu and SO_3+O, while it may be formed by combining CuO with SO_3, or CuO_2 with SO_2, or CuS with O_4. From considerations of this kind chemists have thought it better to employ, as much as possible, what are called synoptic formulæ, which express only the composition

of acids and salts, and not their internal molecular arrangement.

(10.) The anhydrous acids assumed to pre-exist in ternary acids and salts are mostly hypothetical, but those which have an actual independent existence are found to be quite devoid of acid properties, and in their reactions upon various classes of bodies to differ greatly from the corresponding acids. Hence the appellation acid is altogether inapplicable to them, and consequently the phrase anhydrous acid is become gradually disused, and the word anhydride adopted in its stead. The only anhydrides often concerned in chemical reactions are the carbonic, silicic, stannic, sulphurous, and arsenious. With the carbonic and sulphurous anhydrides may be associated carbonic oxide and sulphuric anhydride respectively, as in the following table:—

CO	Carbonic oxide.
CO_2	Carbonic anhydride.
SiO_2	Silica.
SnO_2	Stannic anhydride.
SO_2	Sulphurous anhydride.
SO_3	Sulphuric anhydride.
As_2O_3	Arsenious anhydride.

The carbonic, silicic, stannic, sulphurous, and arsenious acids are unstable, ill-defined bodies, which readily break up into water and the respective anhydrides.

(11.) The general term *salt* is often taken to include the acid, or salt of hydrogen, as well as the salt of a true metal, such as sodium, or of a quasi-metal, such as ammonium. Using the term in this broad sense, it may be said that whenever different salts of different bases or basylides occur in solution, they undergo mutual decomposition to a greater or less extent according to circumstances. Thus when solutions of chloride of hydrogen and nitrate of sodium are mixed together in equivalent proportions, we have produced some chloride of sodium and nitrate of hydrogen together with some unaltered chloride of hydrogen

and nitrate of sodium, or the two salts become four salts, thus:—

$$x\text{HCl} + x\text{NaNO}_3 = y\text{NaCl} + y\text{HNO}_3 + (x-y)\text{HCl} + (x-y)\text{NaNO}_3.$$

But whenever any one of the freshly formed salts is removed from the sphere of chemical action by precipitation or volatilization, there is a complete instead of a partial decomposition, thus:—

$$x\text{HCl} + x\text{AgNo}_3 = x\text{AgCl} + x\text{HNO}_3.$$

Hence we arrive at the following general law. Any two salts which, by an exchange of their respective basylides, can, under the conditions of the experiment, form an insoluble or volatile compound, undergo a complete double decomposition with precipitation of the insoluble or evolution of the volatile compound. Oxalate of calcium, for instance, being insoluble in water, we know that when chloride of calcium solution is mixed with excess of oxalate of ammonium solution, the whole of the calcium will be precipitated in the form of oxalate of calcium, thus:—

$$\text{CaCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 = 2\text{NH}_4\text{Cl} + \text{CaC}_2\text{O}_4.$$

Again, acetic acid or acetate of hydrogen being volatile at a moderate temperature, we know that when acetate of sodium is heated with sulphate of hydrogen a double decomposition will take place, and acetic acid be liberated, thus:—

$$\text{NaH}_3\text{C}_2\text{O}_2 + \text{H}_2\text{SO}_4 = \text{H}_4\text{C}_2\text{O}_2 + \text{NaHSO}_4.$$

As will hereafter be seen, the deposition of characteristic precipitates and evolution of characteristic gases or vapors constitute the most general means by which the presence of particular bodies can be analytically established.

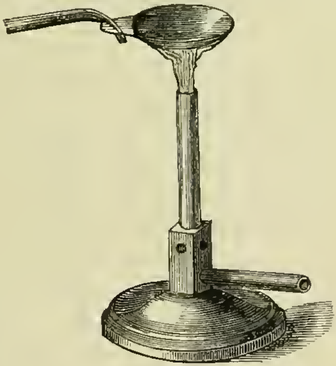
3

§ II.—CHEMICAL MANIPULATION.

(12.) The spirit-lamp is very useful for many operations, especially when a small, smokeless, not over hot flame is required. The charcoal burner is scarcely necessary in a laboratory furnished with gas, but is otherwise almost indispensable. In a chauffer of the kind figured on page 54, one or two places of charcoal may be kept slowly burning, by occasionally blowing off the ash; or a large brisk fire may be kept up, capable of boiling a gallon or more of water. A few pieces of charcoal may also be readily burnt on a coarse wire grating or trellis, resting by its edges on a couple of bricks or other suitable support. But gas is by far the most convenient fuel for ordinary laboratory work. Among burners which are very generally useful may be mentioned the bat's-wing-gauze burner. This consists of a large bat's-wing nipple, screwed into an elbow of brass tube standing on a flat iron foot, and provided with a gallery of some kind to support a brass chimney covered at the top with wire gauze. The bat's-wing flame burnt without the chimney is convenient for bending glass tube, and when reduced by partially turning off the gas, is well fitted for blowpipe testing (Fig. 4). With the chimney on, and the ascending mixture of gas and air burnt at the top of the gauze, as shown on page 50, a large smokeless flame is obtained suitable for heating sand-baths, flasks, test-tubes, &c. An argand burner, screwed into a flat iron foot and provided with a short brass chimney, is also convenient for many purposes, especially when a steady long-continued heat is required. When small flasks, &c., have to be heated, a flat brass ring with an aperture about the size of a shilling may be placed on the top of the argand chimney so as to confine the heat. In the Bunsen burner (Fig. 1), gas issues from a short jet fixed in the interior of an upright tube, having holes at the bottom through which air is sucked in, so as

to produce a mixture of gas and air to be burnt at the top of the tube. The flame is smokeless, and from its great heat well suited for ignitions on a small scale. In many Bunsen burners the gas may be either burnt in a single upright flame, as above described, or in a flat rosette of smaller jets well adapted for evaporations, distillations, &c., as shown on page 52. The Bunsen burner may be further modified by slipping into its upright tube, a somewhat narrower tube, having an expanding, broad, flat opening—the flat flame from which is especially suitable for blowpipe use. Herapath's burner (Fig. 2), is a very useful instrument for effecting strong ignitions or fusions, and for glass working. It consists of a large blowpipe jet *a*, connected with the mouthpiece by a flexible tube, and sliding in the interior of a brass tube *b*, furnished with a supply of gas through a lateral projection *c*, fitting on to an elbow on which it moves easily, so as to allow of the flame being turned in any direction.

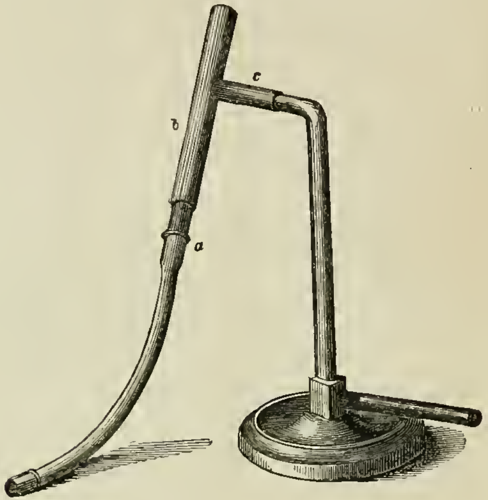
Fig. 1.



(13.) The mode of using the mouth blowpipe, though difficult to describe, is, fortunately, very easy to learn. The best blowpipe for general laboratory use is that designed by Dr. Black (Fig. 3 *a*). It consists of a small conical tube of brass or tin plate closed at its broad, and open at its narrow end, which is usually furnished with a mouthpiece of bone or ivory. From the side of the cone near its broad end, there projects a piece of narrow tube about an inch long terminating in a jet, through which the current of air issues. This jet or nozzle should be turned out

of a solid piece of metal, should be strictly conical both inside and out, and should fit on to the conical

Fig. 2.



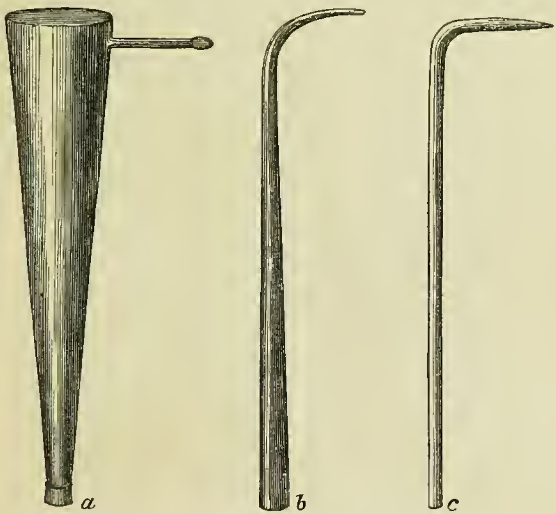
end of the narrow tube by mere pressure without screwing. It is advisable to have a fine jet for testing, and a coarse jet for glass working and general heating; but for these last purposes a common brazier's blowpipe (Fig. 3 *b*), or even a bent glass tube drawn out to a fine point (Fig. 3 *c*), will usually suffice.

A coarse bat's-wing burner with the gas partly cut off, so as to produce a flame scarcely larger than that of a candle, will be found very convenient for blowpipe testing; but in default of gas, the flame of a large candle, or of a spirit lamp fed with solution of turpentine in spirits of wine, may be employed. The candle-wick should be cut of medium length, and turned in the same direction as the blowpipe jet.

In using a blowpipe, the air must be projected by the muscles, not of the chest, but of the mouth, which should be blown out like a trumpeter's. The breath-

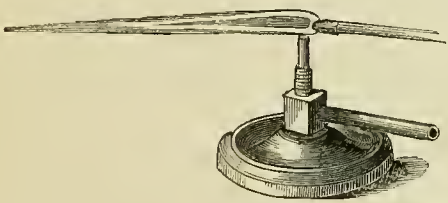
ing has to be carried on through the nose only; and, after a little practice, it will be found easy to keep

Fig. 3.



up a continuous pressure with the cheeks and lips quite unaffected by the alternating respiratory move-

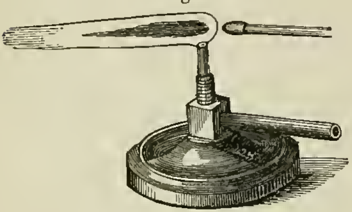
Fig. 4.



ments of the trunk. The mouth should never be allowed to get exhausted of air, but be constantly replenished from behind through the nose. It will be requisite for the student to acquire the power of producing either an oxidizing or reducing flame at

will. To produce an oxidizing flame (Fig. 4), the extremity of the jet should be placed inside the gas, or candle-flame, and a steady not too forcible current of air maintained. By this means, a continuous, silent, lateral flame, of sharply-defined conical form, will be produced. The interior of this flame close to the jet will be dark, and contain an excess of cold air from the mouth; while surrounding it will be seen a somewhat thick layer of clear blue. This is the cone of perfect combustion, the pointed extremity of which constitutes the hottest part of the flame.

Fig. 5.



Outside this blue cone, more especially at its termination, will be perceived a very slightly luminous yellow cone, in which the external air is in excess and at a very high temperature. This constitutes the oxidizing portion of the flame, by exposure to which, a small piece of metallic tin, the size of a pin's head, should gradually swell up into a pulverulent mass of peroxide of tin. To produce a reducing or deoxidizing flame (Fig. 5), the blowpipe jet, which should be rather fine, is placed just outside the gas- or candle-flame, and a somewhat forcible current of air maintained. The resulting blowpipe flame is much less sharply defined than that previously described, and consists principally of a large luminous cone containing an excess of unconsumed carbon, which exerts a powerful reducing action. A minute portion of peroxide of tin, heated in this flame on a charcoal support, may be readily brought to the metallic state even without the use of a flux.

The heating power of the blowpipe flame depends upon the continuous impulsion of hot gaseous matter on to the substance under examination, and upon its rapid removal so soon as it has imparted its heat by

contact. Moreover, a very perfect combustion of the fuel is effected, partly by air projected through the jet, partly by external air drawn in from the sides of the jet and flame, and coinciding in direction with the projected stream.

(14.) Some amount of skill must be attained by the chemical student in constructing apparatus of glass tubing, and in otherwise working with glass. Ordinary tubing or rod may be cut of any required length by making a firm scratch across it with a triangular file, and then breaking it sharply at the file-mark by a conjoint pull and bend. Glass may also be, as it were, sawn through by means of a file, but the operation is rather tedious. It may be much facilitated by occasionally wetting the file with turpentine, or even with water. Glass may be bored through in a similar manner by a drill or a hard bradawl dipped in turpentine. When the neck of a flask, rim of a beaker, or portion of other glass apparatus, becomes cracked, a piece of ignited charcoal, or preferably of pastille, held in contact with the glass immediately in front of the crack, will serve to extend it in any desired direction, so as to cut off the neck or rim, &c. The charcoal may be kept alight by gently blowing on it. Pastilles are made of charcoal powder formed into a mass with thick gum, and rolled into quill-sized sticks, which are dusted with charcoal and dried.

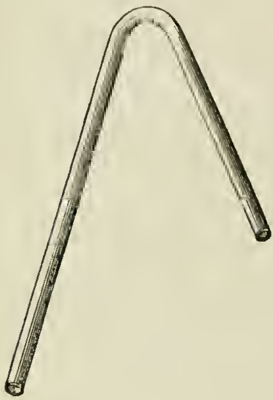
Glass stirring rods are best made from a piece of solid rod or cane long enough for two stirrers. This is to be heated at its middle point in the blowpipe flame, turning it constantly round and gently extending it, until a constriction is formed, which when cold is scratched with a file. The two halves are then snapped apart, and the ends of the stirrers rounded off by directing the flame upon them for a few moments.

Subliming or reduction tubes are made by taking a piece of glass tubing of about 0.2 inch bore and six inches long, heating it at its middle point in the

blowpipe flame until the glass is thoroughly softened, and then gently pulling the two halves asunder. The glass of which these tubes are formed should be clear, thin, and difficultly fusible.

Ordinary glass tubing, unless very thick, may be bent in the flame of a bat's-wing or Bunsen burner.

Fig. 6.



The piece of tubing should be heated over a considerable portion of its length, either at once or successively, and as it gradually softens be bent into the required shape. The production of any constriction in the bore may be avoided by causing some length of tube to take part in the bend, which should never form a sharp angle, but a well-rounded curve, as in the syphon (Fig. 6).

Glass tubing may be drawn out to an almost capillary point, as in the jet of a wash bottle, end of a pipette, &c., by heating a portion of it, about a quarter of an inch long, until it just softens and then steadily pulling until a sufficient constriction is produced, which is afterwards scratched with a file and snapped across. The point may have its edges rounded, and its aperture further diminished if necessary, by holding it in the flame for a few seconds or so. In order to point the extremity of a piece of tubing, another piece of tubing or rod must first be joined to it by the blowpipe, so that the necessary extension may be made. It is often advisable to thicken a tube slightly at the spot where it is to be drawn out, by rotating it for some time in the flame, and gently pressing its ends together. In this way the conical aperture may be made both strong and fine.

(15.) Glass-blowing is a valuable accomplishment

to the practical chemist, but there are only one or two small operations with which it is actually necessary for the student to become familiar. It will be rarely worth while for him to make his own test-tubes, but he should be able to reseal any that have got accidentally broken. By means of the blowpipe, a piece of waste rod or tubing must first be joined firmly on two or three projecting points of the broken end, and be made to coincide as nearly as practicable with the axis of the test-tube, as in Fig. 7. Then, at

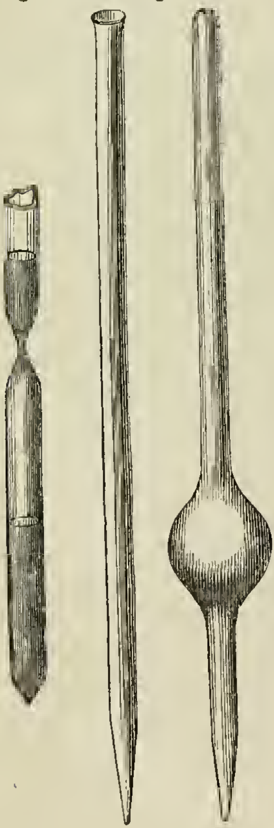
Fig. 7.

about half an inch or more from its broken end, the tube is to be steadily heated in a large blowpipe-flame, and constantly rotated until a considerable constriction is formed, when gentle extension may be employed. The flame is next to be directed upon what will form the bottom of the tube, just at its bend or shoulder, and the extension continued. By this means the end to be pulled away will be left irregularly conical, and that of the new tube well rounded. Finally, the thread of glass proceeding from the cone is to be strongly heated at its junction with the tube until it melts and becomes detached. There is thus always left on the bottom of the tube a little burr or projection of melted glass, which, if sufficiently small, may be made to disappear by heating it and the whole bottom of the tube until the glass is soft, and then blowing into the tube with moderate force while rotating it in the mouth. The burr, if too large for this treatment, may be melted in a small blowpipe-flame, and then have a piece of waste tubing, previously warmed, applied to it, and quickly drawn away, so as to bring the burr with it. In this manner a small burr will be left, which may be melted into the bottom of the tube as above described. The

mouth of a test-tube may be everted by softening it in the flame, and then bending the edge uniformly outwards with the smooth end of an old file previously heated nearly to redness; or else a conical piece of charcoal may be twisted into the softened mouth of the tube.

Glass tubes sealed at both ends constitute the best means of preserving small specimens, either of liquid or solid. One end of the tube is first sealed as if for a test-tube, save that the small burr need not be interfered with. The other end is then constricted to a greater or less extent, according to the size of the specimen to be introduced, so as to leave a funnel-shaped appendage, as in Fig. 8. Liquids may be introduced through a very constricted opening by alternately warming and cooling the body of the tube while the liquid is contained in the funnel. After the substance has been introduced, a small blowpipe-flame is gradually brought to bear upon the constriction, and the sealing completed. Very careful heating is more particularly required when the constriction is moist from the passage of liquid. For practice the student should seal up small tubes filled to within an inch or so of their length with water, spirit, sulphur, sugar, &c. When sealed tubes are

Fig. 8. Fig. 9.



used for effecting reactions under pressure, their ends have to be made with great care so as not to be less resisting than the original sides.

When a small bulb has to be blown upon the end of a piece of tubing, the closed end must first be thickened by rotating it in the flame for some time, and pressing it up with a piece of charcoal until enough glass has accumulated. This thick portion has next to be strongly heated, then withdrawn from the flame, and have air quickly but gently blown into it from the other end, during constant rotation of the tube in the mouth. Or a bulb may be blown in the course of a tube, as in making a bulb pipette (Fig. 9 *b*), for instance. For this purpose a portion of the tube is to be thickened considerably by rotating it in the flame for some time and gently pressing the two ends together. The nearest end is then to be closed with a cork, and the thickened portion, having been strongly heated, is to be distended into a bulb by blowing into the tube at the other end, during its rotation in the mouth. In making a pipette, a strong capillary termination should be first formed, and the bulb afterwards blown. The suction orifice may be everted or not at pleasure. The successful blowing of even small bulbs will not be found easy save after considerable practice.

(16.) Connections of tubing and apparatus are made in various ways. Two pieces of tubing of the same diameter may be sealed together, but the operation requires some amount of skill for its performance. The two ends, well adapted and by preference slightly everted, should be heated to softening in the Bunsen or blowpipe flame, and then brought steadily into contact, taking care that the edges exactly coincide. The junction has then to be heated for some time, constantly rotating the tube, and alternately pushing and pulling the free ends, one of which should be stopped with a cork, and the other occasionally blown into, so as to maintain a proper calibre. A piece of wide may be joined to a piece of smaller tubing, by

first drawing out the former to a point, and then cutting it across just where its diameter coincides with that of the narrow tube. The two can then be joined together as if originally of equal size. In this way funnel-tubes may be made.

Glass tubes of more or less similar diameter are best connected by means of a short piece of vulcanite tubing, the internal diameter of which should be rather less than the exterior diameter of the glass tubes, so as to grasp them firmly by its contraction without requiring to be tied. In the absence of vulcanite, small connectors may be made of sheet India-rubber, a piece of which of the required size is to be gently warmed, and wrapped round a glass rod or tube; when its opposite edges, having been cut obliquely so as to overlap, and firmly pressed together with the thumb-nails, will, if freshly cut and perfectly clean, adhere thoroughly. The removal of the caoutchouc connector, from the tube or rod on which it has been made, may be facilitated by first moistening the rod in the mouth or afterwards dipping it in water. Glass tubes may often be advantageously connected by a considerable length of vulcanite tubing, which can be closed at will anywhere in its course by pressing it together with a clamp of some kind, or even by tying it tightly with a string. A stiff union of two tubes may be made by wrapping a piece of well-soaked bladder or parchment paper several times round their opposed ends, and allowing it to dry on. Or they may be first connected by a piece of vulcanite tubing, and then stiffened by tying on one or two wooden splints made out of lucifer matches. In this way an ordinary funnel may be readily converted into a funnel-tube. An extempore funnel-tube may also be formed by merely resting a small funnel in the suction-orifice of a plain straight pipette (Fig. 9 *a*).

A small tube may be adapted to a considerably larger one, or to the neck of a flask or bottle, by means of a well-fitting perforated cork, the size of which can be readily reduced to any required extent

by rasping and filing. A sound cork of slightly conical shape, and of such a size as to require some little force for its insertion, having been softened by pressure between the fingers or rolling under foot, should be pierced by thrusting the point of a rat-tail file half way through it from each end, and then right through. The hole so made must be enlarged by filing until of a size to fit the tube tightly. When two or more holes have to be made in the same cork, care must be taken to have them all parallel, and as equidistant as possible from one another and from the outside of the cork. For making the necessary perforations variously-sized brass tubes with cutting edges, known as cork-borers, may be used with advantage instead of files. The holes made with them should always be rather too small at first, so as to require some little enlargement by filing. By means of cork-borers, very admirable substitutes for corks may be cut out of solid vulcanite. The end of a tube to be inserted through a perforation should always be rounded off by carefully heating it to redness, so that it may not cut or tear the bore, through which it is, after cooling, to be gradually thrust with a screw-like motion. If fitting very tightly, it may advantageously be greased before its insertion. The cork, with its tube or tubes, is next to be fitted to the neck of the flask or bottle by direct pressure with the fingers and by gentle screwing. That the junction is air-tight may be ascertained by sucking out or blowing into the apparatus, and noticing with the tongue whether any exhaustion, or by the ear whether any compression, is produced. Lutes should be avoided as much as possible, but sealing-wax, varnish, white lead, and linseed meal paste are sometimes useful to stop a leak. Occasionally two pieces of tubing of more or less similar diameter are connected by being each of them inserted half-way through the opposite ends of a long perforated cork.

(17.) By means of glass tubing, vulcanite connectors, and perforated corks, together with flasks,

bottles, or test-tubes, the student may construct for himself a variety of useful apparatus, such, for instance, as the drop-bottle (Fig. 10). From this, when

Fig. 10.

surrounded by the warm hand and inverted, the water or other contained liquid issues in a succession of drops; but when forcibly blown into and quickly inverted, a jet of water springs forth with considerable but gradually decreasing force. This bottle, which should never be more than half filled, is convenient for moistening substances, and for washing down into filters or evaporating dishes the frequently adhering contents of inverted tubes and beakers.

The wash-bottle also (Fig. 11), when held in an upright position and blown into through the short tube, furnishes a fine strong jet of water suitable for washing precipitates; while, upon simple inversion, it delivers a coarse stream of water through the blow-tube, serving to dilute solutions, fill test-tubes, &c. The blow-tube may conveniently be made with a vulcanite joint or mouthpiece, so as to allow some freedom of movement during its use. The jet also may be attached by a cork joint, whereby it can be pointed in any direction. It is convenient to have several wash-bottles, one for cold distilled water, one

made out of a flat-bottomed flask for boiling water, one of smaller size for alcohol, &c. The neck of the

Fig. 11.

hot-water flask should be bound round with list or something of the kind, so as to allow of its being handled. The blow-tube of the alcohol flask may be temporarily closed by a short length of vulcanite, one end of which has been stopped with a bit of glass rod.

Retorts suitable for the generation of gases are readily made by adapting a bent tube and cork to a small flask or test-tube, as in Fig. 12. But when the gas is liberable without the application of heat, a small phial, of such a shape as to stand firmly on the table, may be used instead of a flask. The addition of a funnel-tube is useful when fresh liquid has to be supplied from time to time in order to maintain the effervescence. The bottom of this tube must dip under

Fig. 12.

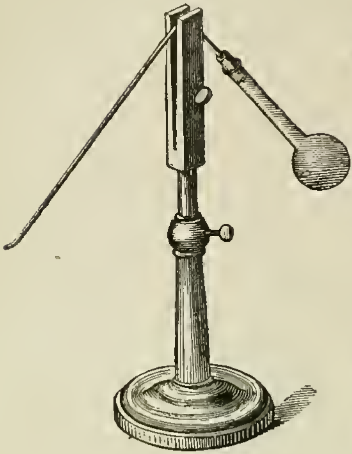
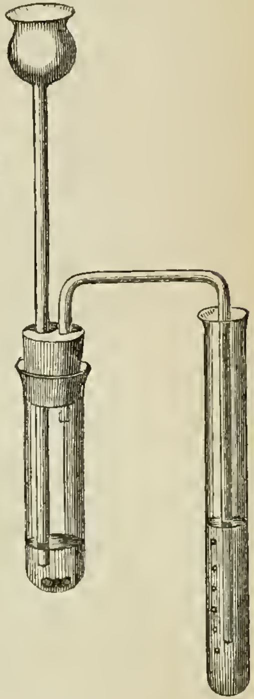


Fig. 13.



liquid in the retort or bottle, so as to be eut off from the liberated gas.

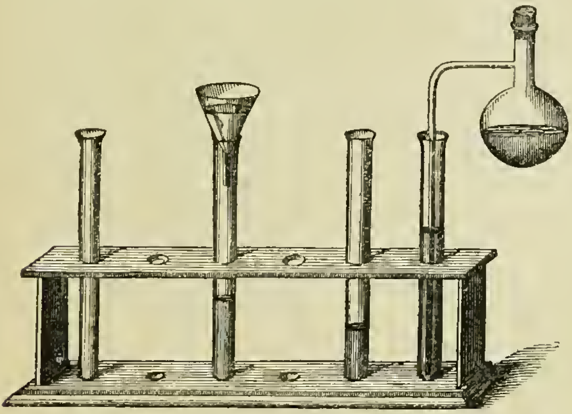
An arrangement of the kind shown in Fig. 13 is useful for testing the nature of a gas generated by the action of a known liquid, usually an aeid, upon some unknown substanee. The acid is poured upon the other substance through the tube-funnel, and the gas eondueted by the bent tube into the test solution, where its effects, if any, are observable.

Gases often require to be purified by aeting on them with certain liquid or solid reagents capable of retaining their different impurities, of whieh aqeous vapor is by far the most eommon. The solid reagent, divided into small pieces, is usually eontained in a glass tube, either straight or bent in the form of the letter U—a little cotton wool or tow being interposed between it and the perforated corks of the tube. The

liquid reagent is either absorbed into pieces of pumice or other porous solid contained in a U-tube, or the current of gas is allowed to bubble up through the liquid contained in a two-necked bottle, or in a wide-mouthed bottle, or in a U-tube, according to circumstances. Most insoluble gases, when required in a pure state, are first washed by their transmission through water, and then dried, if necessary, by being passed over chloride of calcium or pumice soaked in oil of vitriol.

An apparatus for evolving sulphuretted hydrogen gas is indispensable to the analyst. For ordinary testing the generating bulb shown in Fig. 14 is very

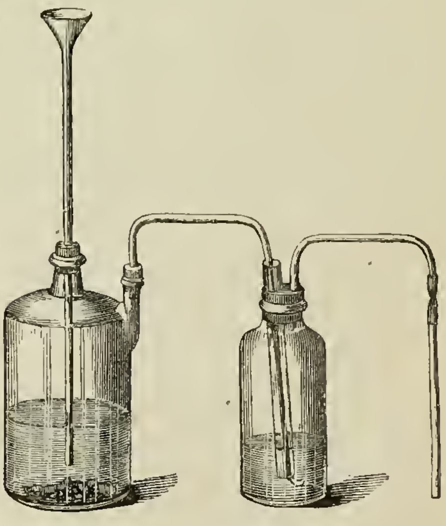
Fig. 14.



convenient. Four or five small lumps of sulphide of iron, not larger than peas, are slid down the neck into the bulb, and covered to some depth with water. Sulphuric acid is then added little by little, until a brisk effervescence is produced, which usually happens when the acid measures about one-tenth part of the water previously introduced. The mouth is then closed by a tightly fitting cork, or even by the thumb, and the evolved gas transmitted through the solution

to be examined. In the absence of the above described bulb, the arrangement shown on page 40 may be employed. The gas from either apparatus may be washed, if necessary, by transmission through a little water contained in a second generating bulb, or in a test-tube, as shown in Fig. 42. But when a continuous supply of washed sulphuretted hydrogen is required, as in some toxicological experiments, a different arrangement is preferable. The gas is developed in a Wolfe's bottle, into one neck of which there passes a tube-funnel, and from the other a delivery-tube bent twice at right angles, which dips through a wider tube into a second bottle charged with a very dilute solution of potash, and furnished with a delivery-tube conveying the gas into the solution to be precipitated, as in Fig. 15. But contriv-

Fig. 15.

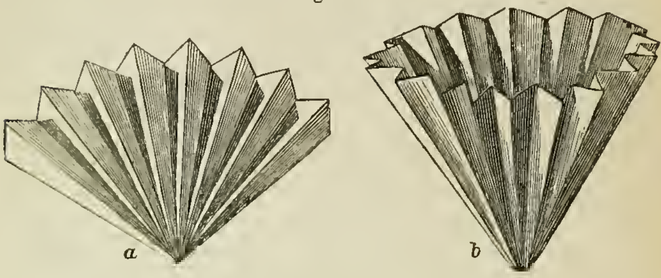


ances of this kind may be infinitely varied, according to the fancy of the operator.

(18.) Filtration is performed in order to separate a mechanically mixed liquid and solid, with a view to obtain the clear liquid which passes through the filter, or the suspended solid which is retained on the filter, or both liquid and solid apart from one another. For analytical purposes, a fine, thin, white blotting paper is employed as the ordinary filtering medium. Boiling water should not dissolve anything from it, and when burnt it should leave scarcely any appreciable ash. It is sold either in sheets, or preferably cut into circles of various sizes. A round or square piece of the paper is folded, in one or other of two ways, into the form of a cone, which, unless very small, should rest in a funnel of glas or fine porcelain. When the object of filtration is merely to clarify the liquid, and especially when such liquid is at all viscid, or requires to be very quickly filtered, as often happens with a hot saturated solution, a ribbed filter is employed. The mode of folding this filter is not easily described, though very easily learnt from demonstration. A circle or square of paper is folded first into halves, then into quarters, and each of the two double quarters again into quarters, all the creases being made on *the same side* of the doubled paper; each sector is next to be divided into two by a crease down the middle made on *the opposite side* of the still doubled paper. At this stage the filter assumes the form of a child's fan (Fig. 16 *a*), and in the event of a square of paper having been used, the projecting ends are to be cut off while the fan is closed. The doubled halves are then for the first time separated, which may be facilitated by blowing on to the edge of the paper, when a deeply ribbed cone will be produced, consisting everywhere of alternate internal and external angles, except at two opposite places where two external angles will be found together, between each of which a subsequent fold must be made, so as to produce an internal angle between them. The filter is now completed, and when gently opened out has the form shown in Fig.

16 *b*. The different creases should be made very sharply at the circumference, but indistinctly at the

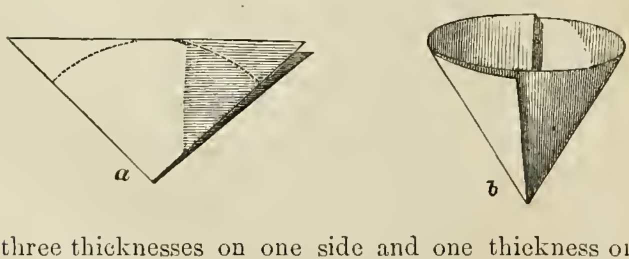
Fig. 16.



centre of the paper for fear of weakening it too much.

But when the chief object of filtration is to collect the suspended matter, most usually a precipitate especially thrown down, a plain filter is much to be preferred. A piece of paper is folded into halves and then into quarters, when it will have the outline of an isosceles triangle, with two straight and one curved side if folded from a circle, or with three straight sides if folded diagonally from a square, in which case the base must be cut round, as shown in Fig. 17 *a*. The filter is then opened out, leaving

Fig. 17.

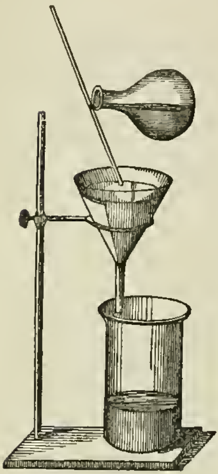


three thicknesses on one side and one thickness on the other, so as to form a smooth cone (Fig. 17 *b*), which is carefully fitted into a funnel in such a man-

ner as to be well supported all round. The funnel should be rather larger than the filter, so as to project somewhat beyond it, while the filter itself should always project beyond the contained liquid. Where it is necessary to employ a double filter, the two should be folded separately, and so arranged in the funnel that the three thicknesses of the one may correspond to the one thickness of the other. The outside filter is often made very small, so as merely to support the bottom of the other. A filter should always be wetted before receiving the mixture to be filtered. This is necessary in order to swell the paper and thereby close its pores, which are otherwise apt to become choked with the precipitate, if indeed some of it be not carried through by the rapid imbibition which at first takes place. When the liquid passes through the paper at all turbid, it should be returned once or twice into the filter, after which it will generally come through clear. It is usually advisable to let the mixture to be filtered subside a little before beginning its filtration. The comparatively clear liquid is then poured off into the filter, and, when it has run through, the thick sediment added separately. The interior of the tube, test-glass or beaker, which contained the mixture, is next to be washed down by a small forcible stream from the wash-bottle, and the rinsings poured on to the deposit left in the filter by the draining away of the previously added liquid. Lastly, by means of a wash-bottle, any deposit extending up the sides of the filter is washed down to its centre, so that the entire precipitate may be collected into as small a bulk as possible for further treatment. It is often necessary, moreover, to wash a precipitate thoroughly, so as to free it from every trace of soluble matter. This is done by projecting water upon it several times by means of the wash-bottle, and allowing the bulk of each addition to filter away before repeating the process, until, on evaporating down a few drops of the filtered washings, no residue whatever is left upon

the slip of glass or platinum foil. The stream of water must not be too forcible, for fear of making a hole in the filter or causing a spirting of its contents. Moreover, in pouring into an empty filter, the liquid should be directed along the side and not immediately upon the point of the filter, which is its most unprotected and consequently weakest part; while the filtered liquid if received in a wide beaker or evaporating dish, should be made to run along the side of the glass or dish, so as to avoid spirting. Again, in pouring from one vessel into another — from a beaker or wide-mouthed flask into a funnel for instance—a glass rod should be applied to the lip of the flask or beaker, as shown in Fig. 18, not only to direct the course of the liquid into the funnel, but also to prevent any of it being spilt by running over the side of the delivering vessel. This running of liquid over the side may also be avoided by greasing that part of the lip which is poured from, with a little tallow or spermaceti ointment.

Fig. 18.



When it is necessary to remove a wet precipitate from the filter on which it has been collected, the well-drained filter, carefully removed from its funnel, may be spread out on two or three folds of bibulous paper to absorb superfluous moisture, and the precipitate be then carefully scraped off from it by a spatula of ivory, platinum, or steel; or the drained filter may be spread out on one side of the funnel, and its contents washed quickly down by a forcible stream from the wash bottle; or by means of a glass rod, a hole may be made in the bottom of a filter *in situ*, and its contents washed through; or the precipitate may be

dissolved off the filter by causing some solvent, usually an acid, to pass through it several times, preferably at a boiling temperature.

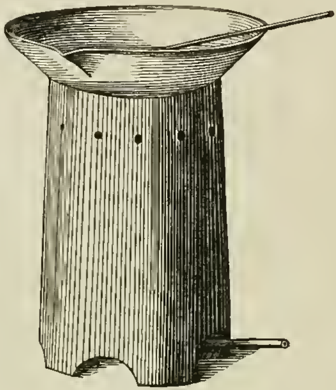
Decantation often furnishes a ready substitute for filtration in cases where the solid part of a mixture has subsided to the bottom of the precipitating glass. The speedy and complete subsidence of a freshly-formed precipitate may often be effected by violently shaking up the mixture for a few minutes in a closed vessel, when, after standing at rest for a little while, the clear supernatant liquor may be poured off with a steady hand, or be withdrawn by a syphon or pi pette. In using a pipette great care must be taken not to allow any of the liquid once sucked up to descend again upon the sediment so as to disturb it. A deposit from which the supernatant liquid has been removed by some form of decantation may be washed by pouring water on to it, stirring it well up, and letting it again subside for a second decantation, and so on. A thin layer of liquid overlying a deposit may often be sucked up very completely by a coil of bibulous paper, introduced with care so as not to disturb the deposit.

Siphons and pipettes are useful not only for separating a supernatant liquid from a deposited solid, but also for separating two strata o 1different liquids from one another.

(19.) Apparatus to be heated over the several burners already described, may, according to its nature, be supported in various ways. It may rest on the ring, or be held by the clamp, of a retort-stand; or an independent upright clamp or tripod stand may be employed. The tripod is often replaced with advantage by a jacket of clay, or metal, surrounding the burner, and so preventing draughts, as shown in Fig. 19. Iron triangles also to rest on the top of the jacket, tripod, or retort-ring, are in constant requisition. A triangle of iron wire, sheathed with three pieces of tobacco-pipe, is useful for supporting small porcelain crucibles that have to be made red-hot, but the mass of

the tobacco-pipe interferes with the attainment of a very high temperature. Small triangles of platinum wire are far more convenient.

Fig. 19.

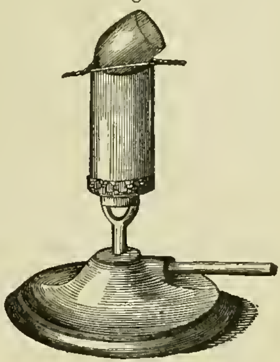


Flasks and retorts may be heated at some little distance over an argand flame without the interposition of any medium. But with the gauze burner, and more particularly with the Bunsen burner, it is advisable to protect the bottom of the vessel by a piece of stout wire gauze. Beakers should be placed either on a flat iron plate or sand-bath, and the heat be raised cautiously. Porcelain evaporating dishes may be heated almost anyhow, according to circumstances; but when the flame touches the bottom of the dish some little care is necessary, both at the commencement of the operation, and when the liquid is evaporated nearly to dryness. Watch-glasses require very careful heating. They are best held by the thumb and finger over a small flame, but may be supported by forceps, wire-triangle, or special watch-glass holder. When containing liquid, to be heated by means of a sand-bath, they should not be depressed into, but just rest on, the top of the hot sand. Test tubes may be readily heated in the flame of a spirit

lamp or gauze-burner. They should be held between the thumb and fingers, and be constantly shaken from side to side, especially during boiling, to prevent any sudden expulsion of the contained liquid, with which they should not be more than half filled. When the boiling has to be long continued, a piece of paper or cloth may be bound or twisted round the upper part of the tube, so as to protect the fingers. Test-tube holders are rarely of much use.

Small capsules and crucibles, of platinum or Berlin ware, may be heated to redness over an argand (Fig. 20) or to full redness over a Bunsen burner, or by the blowpipe flame. They may be held either with forceps or on triangles of wire or tobacco-pipe. When a strong heat is required, they should be surrounded with a small jacket of metal or clay.

Fig. 20.

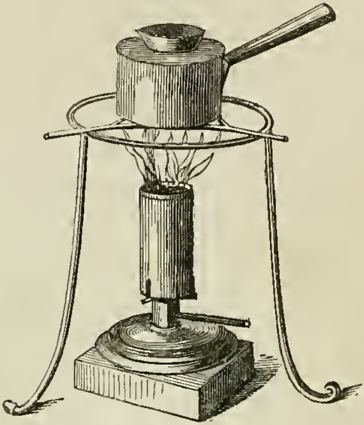


Sand-baths are usually formed of sheet iron. Some are made rather deep to receive flasks and retorts, others nearly flat for beakers. The sand, which must not be heaped above the level of the liquid to be heated, should be of uniform size and rather coarse. An iron plate, or trellis of thick iron wire, forms an excellent substitute for a flat sand-bath.

The water-bath is used for heating substances to a temperature not exceeding 100° C. A small saucepan, with an evaporating dish for a cover, forms a capital makeshift. The saucepan lid may be replaced by a series of broad rings of tin plate, having apertures of different sizes to support small evaporating dishes (Fig. 21), capsules, watch-glasses, necks of flasks, &c. Beakers, flasks, and retorts, to be heated in a water-bath, should not be allowed to touch the bottom of

the bath, but should rest on a piece of tow or folded cloth, as well to avoid danger from bumping as to

Fig. 21.



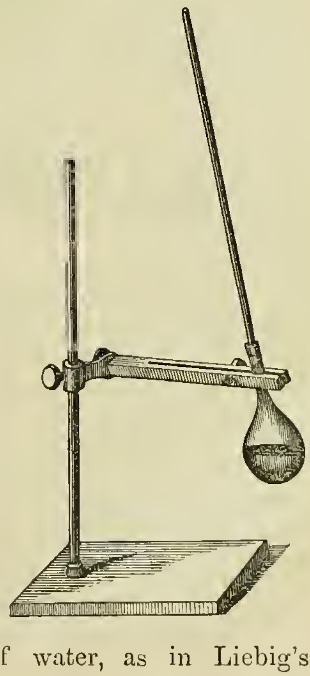
prevent the communication of an increased temperature by contact with the heated metal.

(20.) Heat is applied to liquids in order to warm, evaporate, boil, or distil them. Evaporations are performed on slips of flat glass, or on watch-glasses, or evaporating dishes. The crystalline forms of various salts may often be recognized by dissolving a grain or so of the salt in a drop or two of water on a glass slip, evaporating until a solid margin appears, and setting aside to crystallize. The residue may then be examined by a lens, or under the low power of a microscope. The evaporation of a small quantity of liquid, contained in a watch-glass for instance, may often be promoted by gently blowing on its surface for a little while. A dish in which evaporation is taking place (Fig. 19) may be loosely covered with a piece of filtering paper, stiffened by a glass strip passed through and across it; and care should be taken not to allow the liquid to boil. In evaporating to dryness, it is well to have the heat lowered as the

process approaches completion, and the residue, if considerable, kept constantly stirred.

Ebullition is conducted on a small scale in test tubes, and on a larger scale in flasks—Florence oil flasks being among the best and cheapest that can be employed. A flask of cold liquid, held over a naked flame, quickly becomes covered with a deposit of moisture, which it is advisable to wipe off once or twice. Ebullition sometimes takes place intermittingly, and with considerable jerking or bumping. This may often be prevented by introducing a coil of platinum wire or piece of tobacco pipe into the liquid, either before boiling or after cooling down a degree or two. If introduced during boiling, it is apt to produce a violent rush of vapor. It is occasionally useful to adapt a long upright tube to the mouth of a flask (Fig. 22) in which a liquid has been heated, so that any vapor given off may be condensed in the tube, and flow back again into the flask.

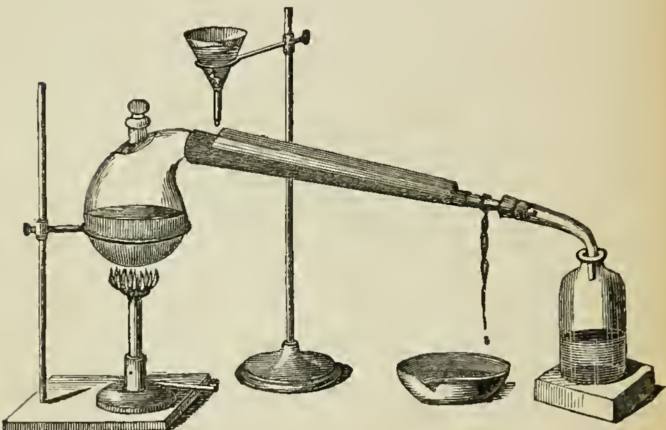
Fig. 22.



Distillation is usually conducted in an apparatus composed of a boiler, condenser, and receiver. On a small scale the boiler is represented by a glass retort, or flask with its bent tube, the receiver by a test tube, flask, or bottle, and the condenser by a long glass tube placed between the retort and receiving flask, and surrounded either by a constantly changing layer of water, as in Liebig's

condenser, or by a piece of blotting-paper kept moist by the constant dripping of water. Very often a separate condensing tube is dispensed with, and the long neck either of the retort or receiving flask alone employed. Fig. 23 shows a very simple arrangement of this description. The liquid is boiled in a long-necked retort, and the distillate conducted by means

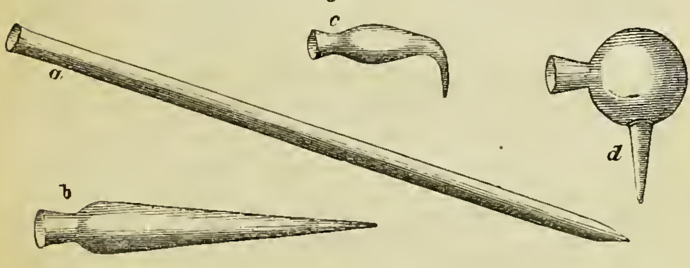
Fig. 23.



of a bent adapter into an upright bottle. A twist of thoroughly wetted tow, or lamp-cotton, is tied somewhat tightly around the retort-neck, at about an inch above the point where it enters the perforated cork of the adapter, and the ends of the twist allowed to hang down for two or three inches. A piece of filtering paper of suitable size and shape to embrace almost the entire circumference of the neck, and reach from just above the twist of tow almost to the curve of the retort, is moistened with water, laid upon the retort-neck and bent round it so as to adhere closely. A second piece of filtering paper is at first folded by means of three creases into four strips, and then placed over the other, so that the flaps being bent

down, its middle portion will form a small channel along the top of the retort-neck. It should be about two-thirds the length of the other, and not reach so high up. By this arrangement the water constantly dropping out of a partly plugged funnel from the height of half an inch or so on to the surface of the inner paper, at a little distance from its upper extremity, is conveyed along the channel, spread uniformly over the retort-neck, and drained away by the twist of tow. If the short length of neck intervening between the twist and adapter be dry at the beginning, it will continue so throughout the experiment. For further security, however, it may be marked with a ring of grease. Adapters are of all shapes and sizes. Such a one as that shown in the woodcut is easily made out of a piece of tubing or broken retort-neck. Others, intended to act more or less as condensers, are represented in Fig. 24. Another convenient form

Fig. 24.

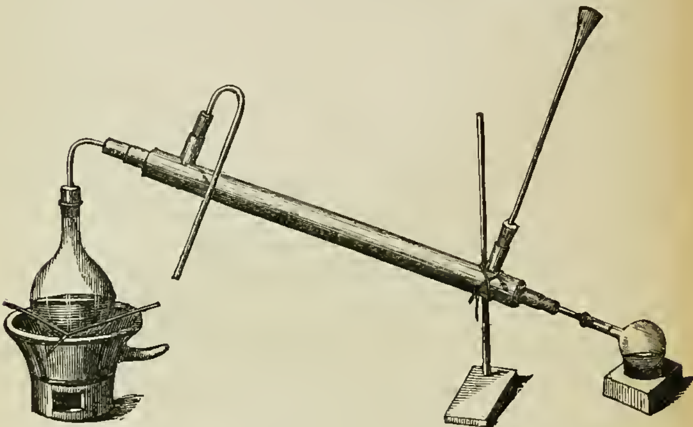


of distilling apparatus is shown in Fig. 40. The boiler consists of a round flask, from which a long wide bent tube dips through a perforated cork into a Florence flask, resting in a basin of water. The cork must either not fit tightly or have a slit cut in it, so as to permit the escape of any uncondensed vapor. The neck and upper surface of the receiving flask should be surrounded with filtering paper, on to which water should drop from a funnel. A bend of

sheet lead may be placed over this flask, so as to sink it in the water.

One of the simplest varieties of Liebig's condenser is shown in Fig. 25. It is merely a cylinder of tin-

Fig. 25.



plate, having four slightly conical tubular apertures—two in the same plane with each other at either side of the cylindrical surface, and two opposite each other in the terminal circular planes. By means of well-fitting perforated corks a funnel tube of tin-plate or glass is inserted into the distant horizontal aperture, and an exit tube of tin or glass into the other, while the distilling tube extends through the axis of the cylinder. The hot contents of the distilling tube pass downwards, becoming colder and colder in their descent, while the stream of cold water entering the condenser through the funnel passes upwards, becoming hotter and hotter in its ascent until it escapes at the overflow pipe. The condenser may be fastened to a retort-stand with string or wire, as in the figure, or may be supported by a clamp of some kind. Liebig's condensers are made in every variety of form, size, material, and construction—some of

them being provided with special supports, which allow them to be heightened or lowered at will, and placed at any desired inclination.

(21.) Heat is applied to solids in order to warm, dry, ignite, fuse, or volatilize them. Any tube, flask, or retort, the interior of which cannot be reached by the fingers, should, after thorough cleaning,* be rinsed once or twice with distilled water, and then drained as dry as possible by means of draining pegs or some other mode of support. It should next be warmed carefully over a gas flame or in front of a fire, and the hot moist air sucked out of it from time to time by the aid of a long tube reaching into it for some considerable distance, as shown in Fig. 26. Narrow

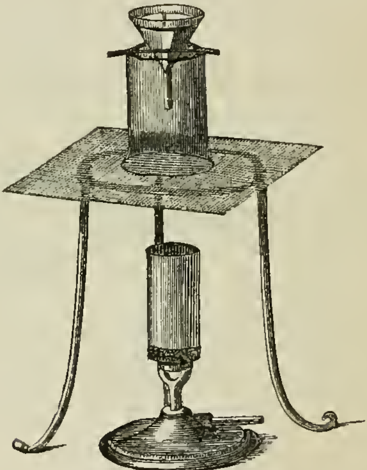
Fig. 26.

glass tubing is dried by heating some length of it over a gas burner or spirit lamp, and simultaneously sucking air through it with the mouth. In the absence of an air or water-oven, reduction tubes and similar small pieces of apparatus may be dried by heating them on a sand-bath standing over a burner; or preferably on a flat iron plate, which in many other cases also may be advantageously substituted for a sand-bath. Moist powders of various kinds may be

* There is seldom much difficulty in cleaning laboratory glass from any stain or dirtiness, when it is not of long standing, by means of cold or hot water and dilute or strong acids or alkalies, aided by extempore brushes made of moist tow dipped in sand and fastened on to thick pieces of wire, or by tube-brushes made specially for the purpose. Flasks, retorts, &c., may often be very efficiently cleaned by shaking them up somewhat violently, after the introduction of a little water and a few pieces of soft paper or rag. The interior of narrow glass tubing is best cleansed by pushing a piece of moist filtering paper through it.

dried on a water-bath, or sand-bath, or by ignition over an argand burner, &c., according to circumstances. A washed precipitate retained in its filter and funnel may often be quickly dried by supporting the funnel on a broken beaker or short lamp-glass standing upon a trellis of iron wire, underneath which a small gas flame is kept burning (Fig. 27). Or the filter may be supported over a heated iron plate by means

Fig. 27.



of a small tripod-stand, easily made out of copper wire. When nearly dry, the filter with its contents may be removed from the funnel and placed in a water-bath; or the washed precipitate and filter may be removed carefully from the funnel, pressed gently between folds of blotting paper, and placed at once in the water-bath. At moderate temperatures, drying over oil of vitriol in the exhausted receiver of an air-pump takes place with considerable rapidity. Moreover, a shallow air-pump jar standing on a plate of ground glass over a dish of oil of vitriol or quicklime,

forms a very convenient chamber in which all sorts of bodies may be dried and kept dry.

Animal solids are frequently subjected to ignition in order to burn off their organic, and leave behind their mineral matter, or ash. The tissue, &c., may be first carbonized in small portions at a time in a thin Berlin capsule or crucible, heated over a gauze burner, in some place where the empyreumatic vapor, &c., can be readily got rid of. The resulting charcoal should then be pulverized, and the powder heated steadily for some hours in a shallow platinum capsule, or on a tray of platinum foil, supported over an argand flame, when the charcoal will gradually burn away, and a white or grayish ash be left. The temperature should never exceed that of dull redness, as otherwise the ash, save that of blood, is apt to fuse over the remaining charcoal, and so prevent its combustion. The operation is much facilitated by protecting the capsule from draughts, and particularly by placing over, but not immediately upon it, a cover of thin platinum foil. Carbonate of sodium and other fluxes employed in testing, are often heated to dull redness over an argand flame just before being used. Moreover, in quantitative analysis, filters and their contained precipitates have constantly to be burnt, with a view of getting rid of the filter-paper and leaving the precipitate in a state fit for being weighed. The ignitions made on charcoal or platinum wire in the course of blowpipe testing will be presently described.

Independently of the many fusions made in the course of blowpipe testing, others on a somewhat larger, though still very small scale, have occasionally to be performed by the student. There are, for instance, a few substances which require to be fused with carbonate of sodium or potassium, either alone or mixed with some other reagent, before they can be brought into a state of solution, and so identified by ordinary analytical processes. The insoluble substance is usually incorporated with three or four times its bulk

of a mixture of carbonate of sodium with carbonate of potassium, or in some cases with either the nitrate or cyanide of potassium, and heated to thorough fusion over a Bunsen or blowpipe flame, in a platinum or porcelain capsule, or in a small iron spoon. In making these fusions, it is most important that both the substance and flux be well dried, very finely powdered, and intimately commixed. The capsule or crucible should be heated at first very gradually, but ultimately to the highest attainable temperature.

The only volatilizations which the student will be called upon to perform are made in narrow glass tubes—open at both ends when a current of air is required to act upon the heated substance, or open at one end only when a simple sublimation is intended. Powdered substances of various kinds may be introduced into narrow tubes open at both ends, by first placing a suitable quantity of the powder in a gutter of stiff glazed paper, pushing this gutter with its contents into the tube held horizontally, then inverting the tube and gutter, and, lastly, withdrawing the gutter while still inverted. The same method may sometimes be used with closed subliming tubes, so as to avoid soiling their interiors, but is unnecessary when both substance and tube are thoroughly dry. The tube, whether open or closed at one end, should be made of hard glass, and be heated in the flame of a spirit lamp or Bunsen burner.

(22.) Although quantitative analysis does not come within the scope of this work, yet a few words on weighing and measuring may not form an inappropriate addition to the foregoing remarks on chemical manipulation. The general adoption of the French metrical system, of which the gramme is the unit of weight, and the cubic centimetre or bulk of a gramme of water at its greatest density the most usual unit of measure, is highly desirable; but in default of this, the English decimal system, of which the standard grain is the unit of weight, and the bulk of a grain of water, at 62° F., the unit of measure, may be em-

ployed. In the chemical laboratory we dispense altogether with the use of ounces, drams, &c., and speak only of so many grammes and cubic centimetres, or grains and grain-measures. Mr. Griffin takes the bulk of seven grains of water as his unit of measure, which he terms a septem, so that 1000 septems are equal to one decigallon, or to the bulk of a pound of water. The use of this decimal division of the gallon is often very convenient, and quite compatible with that of the grain measure, the septem and grain-measure standing to one another in the simple relation of 7 to 1, as shown in the following table. The figures with a dot over them are inexact.

	Decigallons.	Septems.	Grain-measures.
Gallon	......	10,000	70,000
Decigallon or pound	......	1,000	7,000
Quart	2.50	2,500	17,500
Pint	1.25	1,250	8,750
Fluidounce	.0625	62.5	$437.\dot{5}$
Cubic foot	$62.32\dot{1}$	$62,32\dot{1}$	$436,247.\dot{4}$
Cubic inch	......	$36.06\dot{5}$	252.458
Litre	$2.20\dot{4}$	2,204.6	15,432.6
Cubic centimetre	......	$2.\dot{2}$	$15.\dot{4}$

One litre, or kilogramme of water-measure, equals 1.76 pints, or $61.02\dot{7}$ cubic inches. One cubic centimetre, or gramme of water-measure, equals $.06\dot{1}$ cubic inch.

One decigallon or pound of water-measure equals .4535 litre, or $45\dot{3}.5$ cubic centimetres, or $0.016\dot{0}$ cubic foot, or $27.72\dot{7}$ cubic inches, or 16 fluidounces.

Some measures are made to contain or deliver a definite quantity of liquid. Others are graduated

Fig. 28.

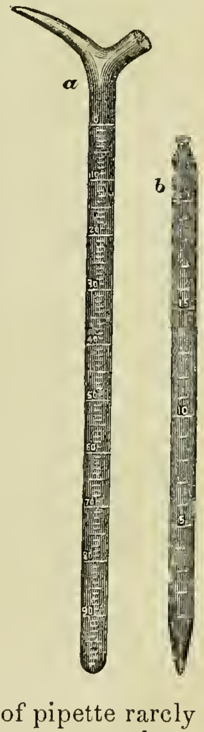
so that any definite quantity delivered may be afterwards read off. A flat-bottomed and somewhat narrow-necked flask, having a horizontal scratch across its neck marking the height to which it should be filled forms a very convenient measure of the former kind (Fig. 28). It is easy to select a couple of such flasks, which shall measure either a decigallon and half-decigallon respectively, or a litre and half-litre, &c. &c. A pipette of the form shown in Fig. 29 is also a very useful instrument of this class. It is filled by carefully sucking up liquid to a level somewhat above the mark on its stem, and quickly closing its upper orifice by the finger. Then by relaxing the pressure of the finger, the contained liquid is allowed to issue drop by drop until its height corresponds exactly with the scratch, when the finger is again pressed down; after which, on removing the finger, the measured quantity of liquid is allowed to flow out. A pipette of this kind is so constructed that when filled up to the mark on its stem it delivers exactly the indicated quantity of liquid, irrespective of what adheres to the interior of its elongated bulb. The last drop should be gently blown out while the point of the pipette is in contact with the inside of the receiving vessel. It is well to have a couple of such pipettes delivering either 100 septems and 10 septems, or 50 and 5 cubic centimetres respec-

Fig. 29.

Fig. 30.

tively. For measuring indefinite quantities a tall narrow cylinder (Fig. 30), graduated into divisions of 10 septems, or 5 c. c. each, is most convenient. The ordinary ounce measures of the apothecary are very unsatisfactory instruments. Their graduation is seldom accurate and always difficult to read off exactly, on account of the expanded conical form of the glass. Where smaller quantities have to be delivered and their volumes afterwards noticed, a Bink's burette of a graduated straight pipette may be employed. The burette (Fig. 31 *a*) should be held near its upper end, with its mouth guarded by the thumb or forefinger, and its beak pointed not directly but obliquely downwards, so that the side of the beak may be inclined to the horizontal plane at a somewhat acute angle. The orifice of the beak should be well greased with tallow or spermaceti ointment, and any liquid remaining in it be sucked down, both at the beginning and end of the experiment. Moreover, the burette must always be allowed to stand at rest for a minute or two before observing the height of the contained liquid. The graduation should be from above to below, as in the woodcut.

Fig. 31.



a *b*

The graduated pipette (Fig. 31 *b*) is filled by suction, the contained liquid adjusted to a proper height, the quantity required allowed to flow out, and the level of the remainder finally read off. Inasmuch as the conical extremity of this kind of pipette rarely delivers its contents exactly, it is better not to have it included in the graduation. Whether the graduation of the pipette is from above to below, or from

below to above, does not much matter; for some purposes the one, and for some purposes the other mode being most convenient.

In reading off the height of a liquid its upper surface should be brought as nearly as possible to a level with the eye. This surface in most liquids contained in glass vessels, will be found more or less deeply concave according to the diametric smallness of the column, &c.; but, in all cases the bottom of the curve is taken as the true level, and, in measuring definite quantities, must be made to coincide exactly with the mark. By right all measurements should be taken at mean temperature, namely, 15.5° C. (60° F.) but the expansions and contractions of aqueous liquids within the ordinary ranges of temperature are so slight that, in most cases, they may be safely disregarded.

A pair of the best description of dispensing scales suspended from a fixed support makes a very useful balance for ordinary work. A set of accurate grain weights ranging from 0.05, or 0.1 grain to 1000 grains should be provided, and also a supplementary short pan for taking specific gravities. The beam should turn freely by an addition of 0.1 grain, even when the pans are each loaded with a weight of twelve or fifteen hundred grains. It is well to employ habitually the left-hand pan for the substance, and the right-hand pan for the weights, which should be always handled by pincers, and not by the fingers. It is sometimes necessary to weigh out definite quantities of a substance such as 20, 50, or 100 grains; but it is better in most cases to take an indefinite quantity and then ascertain its weight, exactly as in weighing any particular specimen, the resultant of an experiment for instance. When taking the weight of an indefinite quantity, much time will be saved by trying the weights not at random but in a definite order, always taking in succession the weight next above or below in the series that particular weight which was last found too little or too much.

It is convenient to provide counterpoises of sheet lead for balancing exactly the several watch-glasses, capsules, crucibles, bottles, &c., used for retaining a substance while being weighed; or their respective weights may be ascertained and scratched upon them. When a definite quantity of substance has to be transferred from the watch-glass or capsule on which it has been weighed into some other vessel, the frequently adhering residue may be washed off by a jet of water, or be gently brushed off by a camel's-hair pencil. But where an indefinite quantity has been taken, it is better to reweigh the watch-glass or capsule and to subtract the weight of adhering residue from the original weight of substance. Or, what comes to the same thing, some portion of a weighed quantity may be transferred, and its amount ascertained by noticing the loss sustained by the originally weighed quantity.

Substances to be accurately weighed must always be first brought to an uniform condition of dryness, inasmuch as a greater or less degree of dryness may cause considerable variation in the weight of a body at different times. The substance may be dried in vacuo over oil of vitriol, or in a water-bath, and its weight determined from time to time until it becomes constant; or, in some cases, the substance may be heated at once to dull redness and then weighed—not, however, until thoroughly cooled, as by resting the containing crucible on a piece of metal, for instance, otherwise an ascending current of heated air will be set up, which will diminish its apparent weight appreciably. Hygrometric substances must be weighed in covered crucibles, or between a pair of ground watch-glasses held together by a clip, or in stoppered bottles made expressly for the purpose, or in short wide test tubes. They may be cooled under a glass jar standing over oil of vitriol.

(23.) By specific gravity is understood the weight of a unit of volume, or, what comes to the same thing, the comparative weights of equal bulks of different

bodies. In this country water at the temperature of 15.5°C. (60° F.) is taken as the standard to which the specific gravities of liquids and solids are usually referred, and its sp. gr. considered either as 1.0 or 1000 according to circumstances.

In order to determine the specific gravity of a liquid, a small flask or bottle of known weight is selected, which, when accurately filled to a certain point, contains a known weight of pure water at 15.5°. This flask is filled with the liquid whose sp. gr. is required, and weighed, when, after deducting the known weight of the flask, the residuary weight of contained liquid is compared with the known weight of the same bulk of water, according to the proportion:—

Wt. of water W' : wt. of liquid W : : sp. gr. of water : sp. gr. of liquid;

that is, according to the equation,

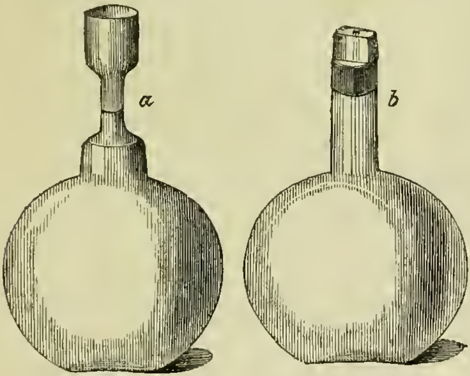
$$\text{Sp. gr. of liquid} = \frac{W \times 1000}{W'}.$$

Thus, supposing the flask to be what is called a five-hundred grain flask, but to contain in reality 499.7 grains of water, and say 459.8 grains of proof spirit, then the sp. gr. of the spirit will be $\frac{459800}{499.7} =$ 920.

Specific gravity flasks or bottles are made of various shapes, one of the most convenient being that employed by Regnault and shown in Fig. 32 *a*, for which, however, any flat-bottomed narrow-necked flask may be substituted. It is to be filled up to the mark on its neck with the liquid, previously brought to the temperature of 15.5° by immersion in cooled or warmed water, and weighed. For taking the specific gravities of very volatile liquids this kind of flask is provided with a solid stopper. The most usual form of sp. gr. flask is shown in Fig. 32 *b*;

when used, it is nearly filled with the liquid to be examined, a tube thermometer introduced, and the whole placed in a vessel of cooled or warmed water until the contained liquid has acquired a temperature

Fig. 32.



of 15.5°. The thermometer is then removed, and the flask filled to the brim with more of the liquid previously brought to mean temperature, the perforated stopper inserted, whereby the excess of liquid is thrust out, and the exterior of the flask thoroughly dried with a cloth, care being taken to avoid any communication of heat from the hand or elsewhere. As a rule sp. gr. flasks should be made perfectly dry before being filled, and by preference be rinsed out with some of the liquid under examination.

The hydrometer (Fig. 33) is useful for taking the specific gravities of different liquids, where rapidity rather than accuracy of determination is required. It is merely an upright float, weighted below, and having a narrow graduated stem above, so as to sink to a greater or less extent in liquids of different densities. Inasmuch as the bulk of any liquid displaced by a floating body is equal in weight to the floating body, it is obvious that equal weights of different

Fig. 33.

liquids will differ in volume according to the depth to which the hydrometer sinks in them; or, in other words, the heights to which different liquids rise on the stem will be inversely as their specific gravities. Some hydrometers, those used in the examination of urine, for instance, are so graduated that their degrees express the specific gravities directly. But in commerce various artificial scales are preferred, that of Twaddell in particular being very generally used in this country. The degree of gravity marked on Twaddell's scale has to be multiplied by 5, and the product added to 1000, to give the actual specific gravity.

The most useful method of taking the specific gravity of a solid body heavier than water, consists in weighing it first in air, or theoretically in a vacuum, and afterwards in pure water at 15.5, when the ratio of the difference in the weighings to the weight in air will give the sp. gr., according to the proportion:—

Dif. in wgs. $W - W'$: wt. in air W :: sp. gr. of water : sp. gr. of solid;

that is, according to the equation

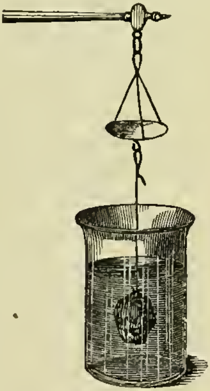
$$\text{Sp. gr. of solid} = \frac{W \times 1.000}{W - W'}.$$

For by a well-known principle in hydrostatics, the apparent loss of weight which a body experiences when immersed in a liquid is identical with the weight of an equal bulk of that liquid.[1]

[1] Relying on this principle, the specific gravities of different liquids may be ascertained by immersing some solid of known weight in each of them, and comparing the losses in weight which it experiences by the upward pressures of the different liquids, equal in each instance to the weight of the bulk of liquid displaced by it.

In order to weigh a solid body in water it must be attached by a horse-hair to the hook of the sp. gr. pan, as shown in Fig. 34, and have its surface thoroughly wetted with a soft brush, so that, when immersed in the water, there shall be no adhering air bubbles. When the solid is soluble in water it must be immersed in alcohol, petroleum, or some other liquid of which the specific gravity has been previously ascertained, and the calculation made as before, substituting the sp. gr. of the liquid employed for the sp. gr. of water. When the solid is lighter than water it must, after its weight in air has been taken, be attached to some heavy body sufficient to sink it, a piece of lead, for instance, and the weight of the solid and piece of lead in water and of the piece of lead alone in water ascertained. The weight of the volume of water displaced by the light solid will equal the weight of the light solid in air W, plus the buoyancy it imparts to the immersed lead, as measured by the difference between the weight of the lead in water w, and the conjoint weight of the lead and light body in water w'. Hence we have the proportion:—

Fig. 34.



Wt. of water $W + w - w'$: wt. of solid W : : sp. gr. of water : sp. gr. of solid;

or the equation:

$$\text{Sp. gr. of light solid} = \frac{W \times 1.000}{W + w - w'}.$$

When the substance to be examined is in the pulverulent state, its specific gravity may be ascertained by means of a sp. gr. flask. A quantity of the powder is introduced into the flask and weighed. It is

then thoroughly wetted with water or some other liquid, of which a further quantity is afterwards added, so as to fill up the flask to the mark on its neck; when the weighing is repeated. The difference between the weight of liquid which the flask ordinarily holds, and the weight of liquid added to fill up the flask after the introduction of the dry powder, gives the weight of the bulk of liquid displaced by the powder, the ratio of which to the weight of the powder gives the specific gravity.

CHAPTER II.

ANALYTICAL CHEMISTRY.

(24.) The object of this part of the course is to make the student practically acquainted with the chemical properties of such bodies as are of the most importance, and of the most common occurrence.

Of all chemical compounds, those known as salts will most frequently present themselves to his notice.

Sulphate of iron and chloride of sodium may be taken as the types of simple salts. The sulphuric acid and chlorine are termed the electro-negative or acid constituents, or, more shortly, the acids; the iron and sodium the electro-positive or basic constituents, or, more shortly, the bases.

In testing the substances distributed for examination, each of which should contain but one basic and one acid constituent, the student may first of all confine himself to the bases; subsequently he must examine both for bases and acids. He will have to pursue the following course of operations:—

I. To examine the dry substance before the blowpipe. (Pars. 25, and 26.)

II. To make a solution of the substance in water or acid. (Pars. 27 and 28.)

III. To ascertain to which group the base of his substance belongs. (Pars. 30, 35, and 41.)

IV. To identify the particular member of the group with which he is dealing. (Tables I., II., and III.)

V. To realize the special reactions described under the head of his particular base.

VI. To identify the acid constituent of his substance. (Tables IV. and V.)

VII. To realize the special reactions described under the head of his particular acid.

As regards V. and VII., the student must remember that the simple discovery of the base and acid of his salt is of much less importance than the thorough verification of all their described properties.

§ I.—BLOWPIPE EXAMINATION.

(25.) A small shallow hole having been made on a piece of charcoal, the student should put into it a little of the substance under examination, a piece about the size of a mustard-seed, for instance, or as much powder as will rest on the point of a penknife. He must then heat the substance on its charcoal support before the blowpipe, and notice what effects, if any, are produced. It is often advisable to moisten a pulverulent substance with water before submitting it to the blowpipe flame, so as to make it cohere and remain on the charcoal. The substance may also be heated with advantage in a subliming tube open at both ends; whereby corroborative, and sometimes even primary, evidence of its composition is obtainable, especially when it happens to be wholly or partly volatile. In this way ammoniacal and sulphurous acid gases may be recognized by their respective smells; deposits of acid or alkaline water, by their reaction to test-paper; and sublimates of sulphur, arsenic, mercury, and ammonium-salts, by their appearance and behavior.

The following are the most important general effects observable upon heating a substance on charcoal before the blowpipe.

All hydrated salts give off their water of crystallization, some with intumescence, as borax; others with decrepitation, as gypsum. Many anhydrous salts also, as chloride of sodium, for instance, decrepitate from the expulsion of water retained mechanically within their crystals. Most hydrated salts, when first heated, fuse in their water of crystalliza-

tion, and then solidify, whether or not susceptible of again fusing at a higher temperature (*vide* par. 26).

Most compounds of the heavy metals become darker when heated, either permanently through decomposition, or temporarily through some altered relation to light. Zinc compounds acquire a deep greenish-yellow by the action of heat, and peroxide of tin a pale brownish-yellow.

Certain metallic compounds, more especially those of silver, lead, and bismuth, are quickly brought to the metallic state when heated on charcoal in the reducing blowpipe flame (*vide* par. 26).

Some substances, whether or not inflammable, leave a black carbonaceous residue, capable of being burnt away by prolonged ignition. This charring indicates the presence of organic matter—an organic acid or base, for instance, either free or in combination.

Many bodies evolve a more or less marked smell when heated. Thus sulphur and many sulphides give off sulphurous anhydride. Tartaric and benzoic acids, and their respective salts, evolve characteristic empyreumatic odors. The fixed organic bases, and some salts of ammonia and organic bases, give off ammoniacal vapor; while arsenic compounds, when in contact with ignited charcoal, give rise to a peculiar garlic-like smell.

Sometimes the heated substance volatilizes wholly or in great measure, usually with evolution of visible fumes (*vide* par. 26).

In a few cases the red-hot charcoal undergoes a rapid combustion where it comes in contact with the heated compound. This deflagration indicates the probable presence of a nitrate or chlorate.

(26.) As regards their more special behavior before the blowpipe, metallic compounds may be classified into those which are volatile (α), those which leave a white permanently fusible residue (β), those which leave a white infusible residue (γ), those which are reducible to the metallic state (δ), and those which give a coloration to the borax bead (ϵ), as shown in the following scheme:—

BLOWPIPE EXAMINATION.

α. Volatile.	β. White and fusible.	γ. White and infusible.	δ. Reducible.	ε. Color borax bead.
AMMONIUM	SODIUM	ZINC	SILVER	CHROMIUM *Green*
MERCURY	POTASSIUM	ALUMINUM	TIN	MANGANESE *Amethyst*
Salts	Salts	MAGNESIUM	LEAD	IRON *Yell'w-brown*
ARSENIC	CALCIUM	CALCIUM	BISMUTH	
Oxides	STRONTIUM	STRONTIUM	ANTIMONY	COBALT *Deep-blue*
Sulphides	BARIUM	BARIUM	CADMIUM	NICKEL *Reddish*
	Chlorides	Salts	*Give incrustations*	
ANTIMONY	*Color blowpipe flame*			COPPER *Pale-blue*
Teroxide		SILICIC	ZINCγ	*In oxidizing flame*
OXALIC ACID		STANNIC	MERCURYα	
		ANTIMONIC	ARSENICα	
		Oxides	COPPERε	

α. The ordinary compounds of **ammonium** and **mercury** are readily volatile. Phosphate of ammonium, however, leaves a fused residue of phosphoric acid, which requires a strong heat for its dissipation. The oxides and sulphides of **arsenic** also are readily volatile; the teroxide of **antimony** somewhat less so. **Oxalic** acid melts and effervesces during its disappearance without furnishing much incrustation. The compounds of mercury, arsenic, and antimony, and many ammonium-salts, deposit incrustations or sublimates upon the cold part of the charcoal. Similar sublimates are procurable by heating the substance in a sealed or open subliming tube.

The various bodies which volatilize when heated on charcoal may often be satisfactorily identified by a few rough tests, such as the following:—

Ammonium salts, when warmed with potash, evolve ammonia, recognizable by its odor and alka-

red sulphide, are turned black by sulphide of ammonium. Mixed with a large excess of carbonate of sodium, and heated in a reduction tube, they afford a sublimate of mercurial globules. The oxides (white) and sulphides (orange or yellow) of **arsenic** dissolve in sulphide of ammonium to form a yellowish liquid, which on evaporation to dryness leaves a bright yellow residue. Mixed with soda-flux, and heated in a reduction tube, they furnish sublimed crusts of metallic arsenic. Teroxide of **antimony** dissolves in sulphide of ammonium, and the liquid, when evaporated down, leaves a deep orange residue. It is, moreover, easily reducible before the blowpipe (δ). **Oxalic** acid, when moistened with water, manifests a strongly acid reaction, and effervesces with peroxide of manganese.

β. The ordinary salts of **sodium** and **potassium** fuse at a red heat, many of them into almost watery liquids, which are absorbed by the porous charcoal. During their ignition, the salts of sodium impart a bright yellow, and those of potassium a violet coloration to the blowpipe flame. These colors are best seen by taking up a minute quantity of the salt upon the end of a platinum wire, and heating it at the point of the blowpipe flame. When a potassium salt is contaminated with even a small proportion of any sodium salt, the violet color of its flame is liable to be concealed by the strong yellow color which the sodium salt produces. But the proper potassium color may be readily seen by looking at the flame through a piece of smalt glass, which cuts off the yellow sodium rays.

Unlike most salts of the alkaline earth-metals, the chlorides of **calcium, strontium,** and **barium** are fusible in the blowpipe flame. That of calcium fuses very readily, but the other two chlorides are much less readily fusible than are the majority of sodium and potassium salts. When strongly ignited on fine platinum wire, chloride of barium imparts to the blowpipe flame a marked apple green, chloride of

line reaction. **Mercury** salts, save the black and strontium a deep crimson, and chloride of calcium an orange-red color. The platinum wire used for testing by the blowpipe flame should be moderately thin, to allow of its being strongly heated. It may be held directly in the fingers, platinum being a bad conductor of heat. Should the end to be used impart any color to the flame, from contamination either with soda, derived from the perspiration of the fingers, or with the residues of former experiments, it must be alternately dipped in hydrochloric acid, and strongly heated in the blowpipe flame until all coloration ceases to appear.

The chlorides of the alkaline earth-metals, and most salts of the alkali metals, fuse into colorless transparent liquids, whereby they are distinguished from the fusible compounds of the heavy metals, which yield colored or opaque beads. Moreover, the temporary melting of hydrated salts in their water of crystallization must not be confounded with the permanent fusion at a red heat which characterizes the above-mentioned classes of salts.

γ. Compounds of **zinc, aluminum,** and **magnesium,** with nearly all **calcium, strontium,** and **barium** salts, whether or not undergoing a preliminary aqueous fusion, leave after strong ignition a white infusible residue; while the **stannic, silicic,** and **antimonic** oxides are from the first infusible. During strong ignition the aluminum residue manifests an intense white incandescence, the zinc residue a deep greenish-yellow, and the stannic and antimonic oxides a pale brownish-yellow color. In any case the white or yellowish-white infusible residue may be moistened with solution of nitrate of cobalt, and again strongly heated, whereby characteristic colorations are produced with compounds of zinc, aluminum, and magnesium, and less definite colorations with the remainder. The **zinc** residue acquires a fine green, the **aluminum** residue a bright blue, and the **magnesium** residue a very faint pink color. When the residue is pulverulent, it may be moistened with sul-

phuric acid and re-ignited before being heated with nitrate of cobalt, more especially in order to bring out the magnesian color. It must be borne in mind that nitrate of cobalt also imparts a blue color to many fused phosphates, borates, and silicates, which, however, cannot be confounded with the blue given to an infusible aluminum residue.

The other infusible residues receive a less distinct color by ignition with nitrate of cobalt, those of calcium and strontium becoming gray, that of barium reddish-gray, those of the stannic and silicic anhydrides bluish-gray, and that of antimony greenish-gray; but these substances may be further distinguished by other means—calcium, strontium, and barium by their tinting the blowpipe flame—antimony and tin by their reducibility, the former with, and the latter without, any incrustation (δ)—and silica by its behavior with fused carbonate of sodium. In order to test an infusible compound for **calcium, strontium,** or **barium,** a small quantity, taken up on the end of a fine platinum wire, should be moistened with hydrochloric acid, and ignited for some time in the hottest part of the blowpipe flame, when the characteristic color due to the volatilization of each metal will be clearly brought out, save indeed with their respective sulphates. **Silica** may be identified by making a small loop at the end of the platinum wire, and fusing upon it a minute quantity of carbonate of sodium, which will thus form a white bead, transparent when hot, opaque when cold: in this fused bead, silica, when strongly heated, will dissolve with effervescence, and, if in sufficient quantity, render it permanently transparent.

δ. Compounds of **silver, tin, lead, bismuth, antimony,** and **cadmium,** often assume the metallic state, or produce characteristic incrustations, when merely heated on charcoal in the reducing blowpipe flame; but their behavior when heated with a flux of carbonate of sodium, mixed or not with cyanide of potassium, is more satisfactory. Carbonate of sodium alone will answer the purpose, but the addition thereto

of one-fourth of its weight of cyanide of potassium often assists the reduction very greatly, and is not in any case disadvantageous, save when the specimen itself deflagrates upon charcoal from the presence of a nitrate or chlorate, in which case a slight explosion results from the reaction of the cyanide and oxisalt.

The specimen having been intimately mixed with five or six times its bulk of flux, a small portion of the resulting powder, sometimes moistened with water so as to make it cohere, is heated strongly on charcoal. The mixed mass should fuse readily before the blowpipe, so that any minute globules of reduced metal may run together. If not readily fusible, a fresh mixture must be taken with a larger proportion of flux. When the reduced metal volatilizes at the temperature employed, its vapor becomes oxidized outside the flame, and is deposited upon the charcoal as a more or less abundant, white or colored, incrustation. Silver gives no incrustation, and tin scarcely any: lead gives a yellow, and bismuth a brownish-yellow, incrustation; while antimony gives an abundant easily volatile bluish-white, and cadmium a comparatively fixed brown-red incrustation. Metallic antimony vaporizes rapidly; while cadmium is so volatile that its reduction and vaporization are simultaneous, wherefore no globule, but only an incrustation, is producible with it. Zinc compounds, heated with reducing flux, behave in this respect like cadmium, furnishing no globule of metal, but only an incrustation, which is yellow when hot, white when cold; but zinc will have been previously detected by its reaction with nitrate of cobalt (γ). Reduced arsenic and mercury are so volatile that they can only be obtained in the form of sublimates by performing the reduction in tubes as already described (α).

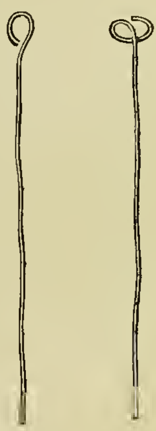
The different metals usually identified by their reduction on charcoal, exhibit the following character: **Silver** yields a bead of white, moderately hard and malleable metal, with no incrustation. **Tin,** which is less easily reducible, yields a bead of white malleable metal, softer than silver, with very slight, if any, in-

crustation. **Lead** yields a bead of soft bluish-white metal, with yellow incrustation; **bismuth**, a bead of brittle yellowish-white metal, with brownish-yellow incrustation; **antimony**, a bead of brittle bluish-white metal, with an abundant bluish-white incrustation; and **cadmium**, no metallic bead, but only a reddish-brown incrustation.

In addition, copper, iron, nickel, and cobalt are reducible, though they do not afford incrustations, and are not easily obtainable in the form of beads. But on crushing the fused mass in a mortar, and washing away the lighter portions, copper may often be recognized in the form of red spangles, and iron, nickel, and cobalt as heavy powders affected by the magnet.

c. Compounds of those metals which tinge the borax bead usually leave dark-colored infusible residues when heated alone on charcoal. In testing the borax bead, a piece of platinum wire is bent into a single or double loop, as shown of the actual size in Fig. 35, the loop dipped into powdered borax, and the adhering borax heated to redness, when it first undergoes a highly characteristic intumescence, and afterwards, when more strongly heated, sinks into a colorless transparent bead. To this bead is then attached a minute quantity of the substance under examination, and the whole strongly heated in the blowpipe flame, when in some cases the fused bead dissolves the specimen, and thereby acquires a more or less definite color, the depth of which may be increased by adding more of the specimen and again heating strongly.

Fig. 35.



The metals **iron** and **copper**, which form two classes of salts, also form beads of two colors. Thus in the oxidizing flame we have a blue

cupric and a yellow-brown ferric bead, while in the reducing flame we have a cuprous bead of an almost colorless or opaque reddish aspect, and a ferrous bead of a sea-green color. The **chromium** bead has an emerald green, and the **cobalt** bead a sapphire blue color. **Manganese,** when free from iron, imparts an amethystine tint, and **nickel** a deep sherry hue, which becomes amethystine when the bead is heated with a fragment of nitre. The borax may be replaced by microcosmic salt, or even by ordinary glass. In these several reagents we have, after ignition, an excess of melted boric, phosphoric, or silicic anhydride, which at the temperature of the blowpipe flame combines with the various metallic oxides to form colored fusible salts.

§ II.—SOLUTION AND PRECIPITATION.

(27.) Having made his examination in the dry way, by means of the blowpipe, the student must next bring his substance, by some means or other, into a state of solution, so that he may submit it to the action of liquid reagents. As a general rule, the substance to be dissolved should be in a finely divided state. This is particularly necessary in the case of bodies which are with difficulty soluble, such as many native oxides, sulphides, &c. Any substance having a decided color, a hard structure, and an opaque aspect, whether earthy or lustrous, ought always to be pulverized very finely before being treated with solvents. The solution of the body under examination should be effected by preference in water; but, if insoluble in water, it may be acted upon with hydrochloric acid, or with nitro-muriatic acid, or with nitric acid.

A small portion of the powdered substance is to be placed in a test-tube, a moderate quantity of **water**[1] added, the whole agitated, and heated over a spirit

[1] By water is always meant pure or distilled water; but clean rain water may sometimes be employed as a substitute.

or gas-flame. While heating, the tube should receive an occasional jerk, to facilitate mixture and avoid the sudden escape of vapor. If the substance, by this treatment, is obviously dissolved, the clear solution, filtered if necessary from any insoluble portions, can be submitted at once to the action of reagents. If the substance, however, is not obviously dissolved, a few drops of the liquid may be filtered on to a glass slip and gently evaporated to dryness. Should any definite amount of residue remain upon the glass, the whole mixture must be thrown upon a filter, and the tests applied to the clear filtrate. There are many substances which, unless taken in very small quantity, do not disappear perceptibly when boiled in water, but yet are sufficiently soluble to afford an aqueous solution that can be successfully tested. Should a mere trace of residue, or none at all, be left upon the glass slip, as much of the water as possible is to be poured away from the insoluble substance, and replaced little by little with **hydrochloric acid**, warming between each addition. Should any obvious action occur, more hydrochloric acid may be added, if necessary, and the whole heated for some time until an available solution is formed. Should there be no obvious action, **nitric acid** must be added in the proportion of about one-fourth of the hydrochloric acid previously used, and heat again applied. By one or other of these means a solution will generally be effected. There are, indeed, a few substances which dissolve in nitric, but neither in hydrochloric nor in nitro-hydrochloric acid. There are also some substances which are quite insoluble in any ordinary menstruum; the consideration of these, however, is deferred for the present. The solution of the substance, whether in water or acid, to which no reagent has been added, is called in the tables and elsewhere *the original solution*. The freshly-made acid solution should generally be diluted somewhat freely with water, and filtered if necessary. The acidity, neutrality, or alkalinity of the aqueous solution should be ascertained by means of test-paper.

(28.) Different reagents are next to be added to the

original solution in the order and manner described in paragraphs 30, 35, and 41, and in the Tables I., II., III., and V. These reagents produce in the solution certain effects, which are characteristic of the various substances dissolved. The effect most usually produced by a liquid reagent is to cause a *precipitate* or solid deposit of some insoluble compound of the substance sought for. Hence the formation or non-formation of a particular precipitate usually proves the presence or absence of a particular base or acid in the solution under examination. Precipitates differ much in their color, consistency, rapidity of formation, and solubility in different liquids, whence the student must make himself familiar with their various aspects and habitudes. As regards aspect, he must notice whether a precipitate is dense, crystalline, clotty, gelatinous, opaque, transparent, colored or colorless, &c. As regards habitude, he will find that crystalline precipitates, unless thrown down from concentrated solutions, do not usually appear at once, but only after some little time. Their immediate formation, however, may be often determined by rubbing the liquid against the inside of the containing vessel with a glass rod. Again, many precipitates are characterized by their solubility in an excess of the precipitant, or in some other reagent.

Reagents and solvents should always be added gradually, except when special direction is given to the contrary. This rule is of great importance, and applies equally to the formation and solution of precipitates; in the latter case, the mixture should be agitated between each addition of the solvent. Many characteristic effects are occasionally overlooked through a neglect of this rule. The student must also bear in mind, when directed to employ an excess of any particular reagent or solvent, that every minute quantity more than sufficient to produce the desired effect is an excess.

In the tables the word *dissolved* placed at the head of a column signifies either that the substances written under it have not been precipitated at all, or

that, having been precipitated, they are now redissolved by an excess of the reagent, in any case that they remain in solution.

EXAMINATION FOR BASIC GROUPS.

(29.) The bases are divided into three principal groups, as follows:—

I.	II.	III.
Tin	Nickel	Barium
Arsenic	Cobalt	Strontium
Antimony	Manganese	Calcium
Bismuth	Iron	Magnesium
Mercury	Chromium	Potassium
Lead	Aluminum	Sodium
Silver	Zinc	Ammonium
Copper		
Cadmium		

The first object of the student must be to ascertain the group to which the base of the salt under his examination belongs.

The members of the first group are precipitated from their acid solutions by *sulphydric acid.* The members of the second group are not precipitated from their acid solutions by sulphydric acid, but are precipitated from their neutral solutions by *sulphide of ammonium.* The members of the third group are precipitated neither by sulphydric acid nor by sulphide of ammonium.

Having ascertained to which particular group the base of his salt belongs, he will proceed according to the directions of the table pertaining to that group, in order to identify the individual member thereof with which he is dealing. Should, therefore, sulphydric acid produce a precipitate, in an acidified solution, the student will proceed according to Table I. Should it produce no obvious precipitate, he will render the solution nearly neutral by ammonia, and then add sulphide of ammonium. Should this reagent produce a precipitate, he will proceed according to Table II. Should no precipitate be produced by either of the above reagents, he will proceed according to Table III.

§ III.—EXAMINATION FOR BASES OF GROUP I.

(30.) To recognize the presence of some member of this group by means of *sulphuretted hydrogen* or sulphydric acid, the solution to be tested should be moderately acid. In solutions which are too acid, sulphuretted hydrogen may not give any precipitate, despite the presence of a member of the group; and in solutions which are neutral or alkaline, it may give a precipitate even in the absence of every member of the group; inasmuch as sulphuretted hydrogen precipitates some members of the second group from their neutral or alkaline solutions.

Aqueous Solutions. These must consequently be acidulated before being treated with sulphuretted hydrogen. A few drops of either nitric or hydrochloric acid will answer the purpose, but the use of the latter acid is generally preferable. The addition of hydrochloric acid, however, sometimes produces a permanent white precipitate, in which case the presence of **silver,** or **lead,** or **mercury** is indicated. Solutions of silver invariably yield a precipitate with hydrochloric acid, solutions of lead and mercury only under certain conditions. But in the event of hydrochloric acid producing a precipitate, it will suffice for the student to distinguish between the above three metals, without following out the directions of the general table for the group (page 85).

The Silver precipitate is soluble in excess of ammonia.

The Mercury precipitate is turned black by excess of ammonia.

The Lead precipitate is unaffected by ammonia, but is soluble in boiling water; and, on cooling, is deposited therefrom in crystalline needles.

These three precipitates are blackened by sulphuretted hydrogen, and are not produced by nitric acid, properties distinguishing them from all other precipitates which hydrochloric acid occasionally produces.

The acidification of a solution of **tartar-emetic,** with either hydrochloric or nitric acid, is attended with the production of a white turbidity, which, however, disappears on gently warming the liquid with a little more acid. Moreover, the acidification, by either hydrochloric or nitric acid, of various alkaline solutions, not unfrequently gives rise to whitish precipitates, which sometimes disappear in an excess of acid, and, at other times, remain. Among those which are permanent, the principal are **sulphur,** from the decomposition of an alkaline persulphide, &c.; **silica,** from the decompositon of an alkaline silicate; and **boric acid,** from the decomposition of an alkaline borate; but this last precipitate is readily soluble in boiling water.

SOLUTIONS IN ACID. When the solution of the original substance has been made in an acid, it is important to get rid of any great excess of acid; or, at any rate, to reduce its activity.

α. **By mere dilution with water.** It is generally advisable to dilute somewhat considerably solutions which have been made by means of an acid.

β. **By evaporation.** The solution may be evaporated down to a small bulk, and then be diluted with water. This process is especially necessary when the solution has been made with nitro-muriatic acid.

γ. **By neutralization with ammonia.** When a large quantity of acid has been employed to effect the solution of a substance, it is occasionally useful to neutralize some of the excess of acid with ammonia.

The acid solution of the substance, whether or not evaporated down, or partly neutralized, should, after dilution with water, be perfectly bright. If not bright, it must be rendered so by filtration.

The addition of water to an acid solution sometimes produces an obvious white precipitate, in which case the dilution should be very slight or be dispensed with altogether. The formation of a white precipi-

tate on the addition of water indicates the presence of ANTIMONY or BISMUTH. The precipitate produced in solutions of the former metal is dissolved by tartaric acid and turned of an orange color by sulphuretted hydrogen; while that produced in solutions of the latter metal is not dissolved by tartaric acid, and is turned black by sulphuretted hydrogen. Water does not invariably cause a precipitate in solutions containing antimony or bismuth, but in the event of a precipitate being produced, it will suffice to distinguish between the above two metals without proceeding according to the general table for the group (page 85).

The acidified solution of the substance in water, or the diluted solution of the substance in acid, is to be treated with sulphuretted hydrogen. It may be sufficient to add sulphuretted hydrogen water to the solution, but it is always preferable to use a current of the gas itself. The production of a colored precipitate is indicative of the presence of some member of the first group; in which case, the gas should be passed into the liquid until it smells permanently even after agitation. A little water should next be added, and the whole well shaken or stirred, to promote the subsequent subsidence of the precipitate, which, on setting the tube aside for a few minutes, will soon collect at the bottom. The supernatant liquid may then be poured off, and the precipitate treated according to the directions of Table I. β.

Sulphuretted hydrogen, when added to certain solutions, not containing any member of the first group, sometimes produces a more or less considerable yellowish-white turbidity, due to a liberation of finely divided sulphur, effected by some per-oxidated or per-chlorinetted compound, thus:—

$$H_2S + Cl_2 = 2HCl + S.$$

In yellow solutions, this white turbidity often appears decidedly yellow, from the color of the liquid through which it is seen. When, simultaneously

with the liberation of sulphur, a brownish-yellow solution becomes paler or colorless, the presence of a **per-salt of iron** may be generally inferred; but when it becomes of a marked green color the presence of **chromic acid** is indicated.

TABLE I.

(31.) Examination of a solution containing some one member of the first group; namely, TIN, ARSENIC, ANTIMONY, BISMUTH, SILVER, MERCURY, LEAD, COPPER, or CADMIUM; all of which metals are precipitated from their acid solutions by *Sulphuretted hydrogen* gas (α), or its solution in water.

β. Having treated the not too acid solution of the substance with excess of sulphuretted hydrogen, and poured off or filtered off the supernatant liquid, warm the precipitate with some solution of *Sulphide of ammonium.*

If the precipitated sulphide be of

- TIN (*protosalt*), brown,
- TIN (*persalt*), yellow,
- ARSENIC, yellow,
- ANTIMONY, orange,

it will *dissolve* entirely, and on addition of hydrochloric acid to the resulting solution will be re-precipitated.

- TIN, always yellow
- ARSENIC, yellow
- ANTIMONY, orange

γ. Boil the precipitate thrown down by sulphuretted hydrogen with strong *Hydrochloric acid.*

Undissolved	*Dissolved*
ARSENIC	TIN ANTIMONY.

If the precipitated sulphide be of

- BISMUTH, SILVER, MERCURY, LEAD, COPPER — black or dark brown,
- CADMIUM, yellow,

it will remain *undissolved.*

δ. Add *Potash* to a portion of the original solution; in any case a precipitate will be produced characterized as follows:—

LEAD, white, *soluble* in excess of the reagent, unaffected by ammonia.

Insoluble in excess of potash:

- MERCURY (*protosalt*), black, unaffected by ammonia.
- MERCURY (*persalt*), yellow, turned white by ammonia.
- BISMUTH, white, unaffected by ammonia.
- COPPER, blue; CADMIUM, white; SILVER, brown — Soluble in ammonia.

(32.) *a. Sulphydric acid*, or *sulphuretted hydrogen*, reacts with the salts belonging to this group to form metallic sulphides, as shown by the following typical equations, in which M stands for an atom of metal:—

$$2\overset{\prime}{M}Cl + H_2S = 2HCl + \overset{\prime}{M}_2S$$
$$2\overset{\prime\prime\prime}{M}Cl_3 + 3H_2S = 6HCl + \overset{\prime\prime\prime}{M}_2S_3.$$

In this manner the salts of perissad metals, as silver Ag', arsenic As''', antimony Sb''', and bismuth Bi''', are decomposed by sulphuretted hydrogen.

$$\overset{\prime\prime}{M}Cl_2 + H_2S = 2HCl + \overset{\prime\prime}{M}S$$
$$\overset{\prime\prime\prime\prime}{M}Cl_4 + 2H_2S = 4HCl + \overset{\prime\prime\prime\prime}{M}S_2.$$

In this manner the salts of artiad metals, as lead Pb'', mercury Hg'', copper Cu'', cadmium Cd'', tin (stannosum) Sn'', and tin (stannicum) Sn'''' are decomposed by sulphuretted hydrogen.

The sulphides thus produced differ much from one another as regards their solubility in mineral acids. They are all completely dissolved by **nitro-muriatic acid**; except that of silver, which is converted into insoluble chloride of silver; and that of lead, which is converted partly into the sparingly soluble chloride, partly into the insoluble sulphate of lead, owing to an oxidation of its constituent sulphur.

Hot **nitric acid** dissolves the sulphides of arsenic, bismuth, silver, copper, and cadmium, but has no appreciable action on the sulphides of mercury. It converts the sulphides of tin and antimony into their insoluble oxides or anhydrides, SnO_2 and Sb_2O_4 respectively. When slightly diluted, it dissolves sulphide of lead completely, but otherwise it converts a portion of it into insoluble sulphate of lead. The action of nitric acid upon the sulphides is generally attended with a separation of sulphur, which, on boiling, gradually assumes the form of melted globules.

Strong **hydrochloric acid** at a boiling temperature has no action on the sulphides of arsenic and mercury. It converts the sulphides of silver and lead

into their insoluble or sparingly soluble chlorides, and dissolves the remaining sulphides of the group with greater or less facility.

(33.) β. The disulphide of tin, and the trisulphides of arsenic and antimony, unite with the sulphides of alkali-metal to form soluble sulphur-salts corresponding to the well-known oxygen salts, thus:—

Ammonium sulpho-salts.

$$(NH_4)_2S.SnS_2 \quad = \quad (NH_4)_2SnS_3$$
$$3(NH_4)_2S.Sb_2S_3 \quad = \quad 2(NH_4)_3SbS_3.$$

Hence these sulphides are distinguished from the remainder by their solubility in *sulphide of ammonium*.* Protosulphide of tin is not soluble in pure colorless sulphide or sulphydrate of ammonium; but it is soluble in the ordinary yellow solution of the persulphide, whereby it becomes converted into the above-described compound of disulphide of tin, thus:—

$$(NH_4)_2S_2 + \overset{\prime\prime}{Sn}S = (NH_4)_2S.\overset{\prime\prime\prime\prime}{Sn}S_2 \quad \text{or} \quad (NH_4)_3SnS_3.$$

On the addition of hydrochloric acid to any of these sulpho-salts, they are decomposed with reprecipitation of their respective sulphides, thus:—

$$(NH_4)_2S.SnS_2 + 2HCl = H_2S + SnS_2 + 2NH_4Cl$$
$$3(NH_4)_2S.As_2S_3 + 6HCl = 3H_2S + As_2S_3 + 6NH_4Cl.$$

It is advisable not to dissolve the sulphides of this sub-section in an unnecessarily large quantity of yellow sulphide of ammonium, lest the subsequent addition of hydrochloric acid should separate so great a quantity of whitish sulphur as to conceal the color of the reprecipitated sulphides.

γ. Sulphide of arsenic is distinguishable from the sulphides of tin and antimony by its insolubility even in boiling hydrochloric adid; and by its solubility in a warm solution of sesquicarbonate of ammonia.

* Sulphide of copper is quite insoluble in the sulphides of sodium and potassium; but is slightly soluble in sulphide of ammonium, especially when it contains, as it usually does, some free ammonia.

Sulphide of antimony and persulphide of tin are distinguishable from one another by their difference in color. When pure they dissolve completely in hydrochloric acid; but as usually obtained they often contain excess of sulphur, which remains undissolved. Upon evaporating down their hydrochloric acid solutions to a small bulk, stannic and antimonious chlorides are obtained respectively. The former chloride does not have its transparency affected by dilution, neither does the diluted liquid yield any deposit upon a surface of metallic tin: and again, an acid solution of chloride of tin, in which a small fragment of zinc has been dissolved, gives with corrosive sublimate a white precipitate of calomel, gradually becoming gray from its conversion into metallic mercury (vide par. 34).

The latter chloride is generally rendered opaque by diluting its solution, which again becomes clear on the addition of tartaric acid; while the diluted liquid yields an abundant black deposit of pulverulent antimony upon a surface of metallic tin. Moreover, chloride of antimony reacts satisfactorily when examined by Marsh's or Reinsch's process.

Solid compounds of arsenic are most readily recognized by the reduction test (vide par. 66).

(34.) δ *Potash* reacts with the salts belonging to the second section of this group, to precipitate the hydrated oxides of the respective metals, thus:—

$$2\overset{\prime}{Ag}Cl + 2KHO = 2KCl + Ag_2O \,.\, H_2O$$

$$2\overset{\prime\prime\prime}{Bi}Cl_3 + 6KHO = 6KCl + \overset{\prime\prime\prime}{Bi}_2O_3.3H_2O.$$

The hydrated oxides of mercury, lead, copper, and cadmium are produced according to the following general equation:—

$$\overset{\prime\prime}{M}Cl_2 + 2KHO = 2KCl + MO.H_2O.$$

Hydrate of lead is soluble in excess of potash; the hydrates of silver, copper and cadmium are soluble in excess of ammonia; while those of bismuth and

mercury are insoluble in either reagent. Independently of their behavior with sulphuretted hydrogen and caustic alkalies, the metals of this sub-section of the first group are characterized by the following reactions.

Bismuth solutions, unless too acid, when they must first be evaporated down, yield an opaque white precipitate on the addition of *water*, due to the formation of some insoluble basic salt, thus:—

$$\overset{'''}{Bi}Cl_3 + H_2O = 2HCl + \overset{'''}{Bi}OCl$$

$$Bi(NO_3)_3 + H_2O = 2HNO_3 + BiO.NO_3 \text{ or } \tfrac{1}{2}(Bi_2O_3.N_2O_5).$$

These basic salts of bismuth are insoluble in tartaric acid, and are blackened by sulphuretted hydrogen or sulphide of ammonium.

Mercury solutions yield with *protochloride of tin* a white precipitate becoming gray spontaneously, or more rapidly on the application of heat. The white precipitate is calomel, which is formed from mercurious salts by double decomposition, thus:—

$$2HgNO_3 + \overset{''}{Sn}Cl_2 = 2HgCl + \overset{''}{Sn}(NO_3)_2 \text{ or } SnO.N_2O_5.$$

But it is formed from mercuric salts by reduction, thus:—

$$2HgCl_2 + \overset{'}{Sn}Cl_2 = 2HgCl + \overset{'''}{Sn}Cl_4.$$

The gray deposit consists of finely divided metallic mercury, produced by an abstraction of chlorine from the calomel first precipitated:—

$$2HgCl + \overset{''}{Sn}Cl_2 = Hg_2 + \overset{''''}{Sn}Cl_4.$$

This gray deposit, when boiled with hydrochloric acid, acquires the characteristic appearance of globules of mercury.

Lead solutions yield with *sulphuric acid*, or soluble sulphates, a white precipitate of sulphate of lead, insoluble in cold nitric or hydrochloric acid:—

$$\overset{''}{Pb}(NO_3)_2 + H_2SO_4 = 2HNO_3 + \overset{''}{Pb}SO_4 \text{ or } PbO.SO_3.$$

The precipitate is distinguished from the similar precipitate produced with barium- and strontium-salts, by its solubility in excess of potash, by its solubility in boiling hydrochloric acid, and by its becoming blackened by sulphuretted-hydrogen or sulphide of ammonium.

Silver solutions yield with *hydrochloric acid* or soluble chlorides a white clotty precipitate of chloride of silver:—

$$AgNO_3 + HCl = HNO_3 + AgCl.$$

The precipitate is soluble in ammonia, but insoluble in the strongest nitric acid, even when boiling. It is turned of a slate-purple color by exposure to light.

Copper solutions, even when very dilute, give with *ferrocyanide of potassium* a chocolate-red precipitate of ferrocyanide of copper, or of ferrocyanide of copper and potassium, thus:—

$$2\overset{\prime\prime}{Cu}SO_4 + K_4FeCy_6 = 2K_2SO_4 + \overset{\prime\prime}{Cu}_2FeCy_6.$$

The precipitate is turned of a pale blue color by potash, and is then readily soluble in ammonia, forming a deep purple colored liquid, by which properties it is distinguished from the similarly colored ferrocyanide of uranium.

Cadmium solutions are specially recognized by the bright yellow color and insolubility in sulphide of ammonium, of the precipitated sulphide of cadmium CdS, produced by sulphuretted hydrogen or sulphide of ammonium. Of all the sulphides of the first group of metals, sulphide of cadmium is the one most readily soluble in acids. Cadmium-salts, moreover, are readily identified by their behavior before the blowpipe.

§ IV.—EXAMINATION FOR BASES OF GROUP II.

(35.) The members of this group are precipitated by *sulphide* or *sulphydrate of ammonium*, but are not

precipitated from their acidified solutions by sulphuretted hydrogen. Inasmuch as sulphide of ammonium also precipitates most of the metals of the first group, their absence must be ascertained by the non-production of a precipitate with sulphuretted hydrogen, before the reaction with sulphide of ammonium can be depended on as a general test for members of the second group.

The solution to be tested with sulphide of ammonium should be nearly neutral, but it may be slightly alkaline, or slightly acid without disadvantage. It must not, however, be decidedly acid; for if so, there may not only be no precipitate produced when some member of the group is present, but owing to a customary impurity in the reagent, there may even be a precipitate produced when every member of the group is absent. This last occurrence is consequent upon a deposition of sulphur from the mutual decomposition of the acid solution and the reagent, quite irrespective of the presence of any metal. Pure colorless sulphide or sulphydrate of ammonium, indeed, is not precipitated by mere acid solutions; but the yellow persulphide of ammonium, into which it becomes gradually converted, is decomposed by all acid liquids with precipitation of sulphur, thus:—

$$2HCl + (NH_4)_2S_2 = 2NH_4Cl + H_2S + S.$$

The aqueous solution of a salt may be examined for members of the second group, by adding sulphide of ammonium at once; but a solution of the salt in acid must be rendered neutral, or nearly neutral, with ammonia before applying the test. The addition of even an excess of ammonia to the acid liquid is no disadvantage. It will sometimes, indeed, produce a precipitate, but the formation of a precipitate by ammonia, equally with the formation of a precipitate by sulphide of ammonium, indicates the presence of a member of the second group; though the non-production of a precipitate by ammonia does not prove the absence of all members of the group. The pre-

cipitate produced by ammonia generally differs in its character, and frequently in its appearance, from that produced by sulphide of ammonia, but the formation of a precipitate by ammonia will not interfere with the action of the more characteristic reagent for the group.

The acidulous solution of the substance which has been tested with sulphuretted hydrogen, but which has not yielded any precipitate therewith, may be examined for members of the second group by treatment with ammonia. In this case, one portion of the ammonia neutralizes the excess of acid, while another portion combines with the sulphuretted hydrogen to form sulphide or sulphydrate of ammonium, which serves to precipitate any member of the group, thus:—

$$H_2S + 2NH_3 = (NH_4)_2S.$$

There are certain salts of barium, strontium, calcium, and magnesium which do not dissolve in water, but which are readily soluble in dilute mineral acids —nitric or hydrochloric, for instance—without, at the same time, undergoing any obvious decomposition. Hence, when such an acid solution is neutralized by ammonia, or by sulphide of ammonium, the salts are reprecipitated in their original condition; so that, although the alkaline earths strictly belong to the third group, they are occasionally precipitated along with the proper members of the second. These salts are principally the **fluoride** of **calcium**—the **oxalates** of **calcium, strontium,** and **barium**—and the **phosphates** of **magnesium, calcium, strontium,** and **barium.** In Table II. they are referred to under the general term of earthy salts; and the mode of distinguishing them from one another is described in par. 59.

Table II.

(36.) Examination of a solution containing some one member of the second group of bases; namely, Nickel, Cobalt, Manganese, Iron, Chromium,

ALUMINUM, or ZINC; all of which bodies are precipitated by *Sulphide of Ammonium* (α), from their neutral, or nearly neutral, solutions.*

β. Add gradually a considerable excess of aqueous *potash* to a portion of the original solution. In any case a precipitate will be formed, which may either remain or be redissolved.

- *Undissolved*
  - NICKEL, pale green.
  - COBALT, pale blue.
  - MANGANESE, white, becoming brown.
  - IRON, olive-green, black, or red.
  - EARTHY SALTS, white.

  γ. Add to a fresh portion of the original solution some *chloride of ammonium* and an excess of *ammonia*.

  - *Precipitated*
    - IRON, red
    - EARTHY SALTS, white.
  - *Dissolved*
    - NICKEL, blue.
    - COBALT, brownish pink.
    - MANGANESE, colorless, speedily becoming brown and turbid.

- *Dissolved*
  - CHROME, green.
  - ALUMINUM, white.
  - ZINC, white.

  δ. *Boil* the potash solution for some time.

  - *Precipitated*
    - CHROME, green
  - *Dissolved*
    - ALUMINUM.
    - ZINC.

    To the potash solution

    - ε. Add a few drops of *sulphide of ammonium*.
      - *Precipitated*
        - ZINC.
    - ζ. Add excess of *chloride of ammonium*.
      - *Precipitated.*
        - ALUMINUM.

(37.) α. *Sulphide of ammonium* reacts with salts pertaining to this group, to form precipitates of various

* To work successfully, the student must supplement the brief directions of the different tables, and more especially of this table, by the explanations and limitations of the succeeding letterpress.

characters and aspects. The precipitate is white in solutions of zinc, aluminum, and the earthy salts; black in solutions of iron, nickel, and cobalt; greenish in solutions of chrome; and buff-colored in those of manganese. The student must not, however, attach too much importance to the color of a precipitate, as it is a quality very liable to be interfered with by accidental circumstances. For instance, the presence of a trace of iron occurring as an impurity, may effect a great alteration in the characteristic appearance of precipitates due to chrome, manganese, zinc, aluminum, or earthy salts, respectively, by imparting to them a black, gray, or greenish color. From its transparency, the precipitate produced in aluminous solutions is very liable to be overlooked.

The salts of nickel, cobalt, manganese, iron and zinc are precipitated by *sulphide of ammonium*, in the form of sulphides, according to the general equation,

$$\overset{''}{M}Cl_2 + (NH_4)_2S = 2NH_4Cl + \overset{''}{M}S.$$

From their neutral solutions these metals are precipitated very imperfectly by sulphuretted hydrogen, in consequence of the formation during the reaction of hydrochloric or some other acid, in which the respective sulphides are soluble, thus:—

$$\overset{''}{M}Cl_2 + H_2S = 2HCl + \overset{''}{M}S.$$

But the sulphides of nickel, cobalt and zinc may be precipitated completely from solutions which are acid only with acetic acid, and in which, owing to the addition of an alkaline acetate, no stronger acid than the acetate can be set free during the reaction; though even then sulphide of iron can be but partially precipitated, and sulphide of manganese not at all.

Although the sulphides of nickel and cobalt are not precipitated in the presence of hydrochloric acid, yet, when once produced, they can only be dissolved in the acid with considerable difficulty; but they are readily soluble in nitric acid. The sulphides of zinc, iron, and manganese, however, are easily dissolved

by cold hydrochloric acid, and that of manganese by acetic acid.

The sulphides of aluminum and chromium cannot be produced in the moist way. Hence the salts of these metals are precipitated by sulphide of ammonium in the form, not of sulphides, but of hydrated sesquioxides, with liberation of sulphuretted hydrogen, thus:—

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 6NH_4Cl + 3H_2S + Al_2O_3.3H_2O.$$

The earthy salts are precipitated as such by a mere neutralization of the acid in which they were dissolved, thus (vide page 92):—

$$Ca_3(PO_4)_2 . 4HCl + 2(NH_4)_2S = Ca_3(PO_4)_2 + 4NH_4Cl + 2H_2S.$$

(38.) β. From protosalts of nickel, cobalt, manganese, iron, and zinc, *potash* throws down the respective prothydrates, precisely as it does the prothydrates of the metals of the first group:—

$$\overset{''}{M}Cl_2 + 2KHO = 2KCl + \overset{''}{M}O.H_2O.$$

From the tri- or sesquisalts of iron, chromium, and aluminum, it precipitates the respective sesquihydrates, thus:—

$$2MCl_3 + 6KHO = 6KCl + \overset{'''}{M}_2O_3 . 3H_2O.$$

The earthy salts are precipitated as such by the neutralization of the acid in which they were dissolved.

The appearance of the manganese precipitate is very characteristic. From being quite white it becomes rapidly brown by an absorption of atmospheric oxygen. The precipitate given by potash with perfectly pure protosalts of iron is greenish-white, but the precipitate ordinarily obtained has a dark olive-green color, becoming ochrey-red by exposure to air; with mixed proto- and sesqui-salts, a black precipitate, and with pure sesqui-salts a red-brown precipitate is produced. The hydrates of chromium, aluminum, and zinc are completely soluble in excess of potash,

while the other precipitates are insoluble. Should the excess of potash effect an obvious solution of the precipitate at first thrown down, but the liquid at the same time not become perfectly bright, it may be filtered off from the oxide of iron, or other insoluble impurity, and tested for chromium, aluminum, and zinc (δ.)

(39.) γ. *Ammonia* throws down from solutions of **nickel, cobalt, manganese, iron,** and **earthy salts,** precipitates which have respectively the same composition as those thrown down by potash. The precipitates produced in solutions of the earthy salts and in sesquisalts of iron are equally insoluble in excess of ammonia as in excess of potash; but the prothydrates of nickel, cobalt, and manganese are readily soluble, and that of iron sparingly soluble, in excess of ammonia, when chloride of ammonium, or some other neutral anatomical salt, is also present. Hence when the previous experiment with potash has shown the probable presence of a protosalt of iron, it is necessary, before adding ammonia, to boil the solution with a little nitric acid for a few minutes, so as to convert the protosalt into a sesquisalt, whereby all the iron may be precipitated as a red-brown sesquihydrate, quite insoluble in excess of ammonia.

But when the color of the precipitate produced by potash, or some other reaction, has indicated the absence of a protosalt of iron, the boiling with nitric acid may be dispensed with. The presence of a **protosalt** of **iron** in the original solution is best shown by the addition of *ferridcyanide of potassium*, which produces therewith an abundant dark blue precipitate of ferridcyanide of iron, or Turnbull's blue:—

$$3\overset{''}{Fe}Cl_2 + 2K_3\overset{'''}{Fe}Cy_6 = 6KCl + \overset{''}{Fe}_3\overset{'''}{Fe}_2Cy_{12}.$$

The presence of a **sesquisalt** of **iron** is best shown by *sulphocyanate of potassium*, which produces therewith a blood-red liquid, due to the formation of sesqui-sulphocyanate of iron:—

$$\overset{'''}{Fe}Cl_3 + 3KCyS = 3KCl + \overset{'''}{Fe}(CyS)_3.$$

The mode of examining the **earthy salts** is described in par. 59.

When excess of ammonia is added to a strongly acid solution, or when chloride of ammonium and excess of ammonia are added to a nearly neutral solution of nickel, cobalt, or manganese, the precipitate at first produced is immediately redissolved.

The ammoniacal solution of **nickel** has a deep purple-blue color, closely resembling that of the similarly constituted solution of copper. Potash added to the ammoniacal solution, throws down an apple-green precipitate of hydrate of nickel; but a very large quantity of potash may be added to the ammoniacal copper solution without disturbing its transparency, and the precipitate finally produced is for the most part blue. Moreover, ferrocyanide of potassium produces, with ordinary salts of nickel, a pale green, and with ordinary salts of copper a chocolate-red, precipitate of the respective ferrocyanides; and the two metals are otherwise well characterized.

The ammoniacal solution of **cobalt** has a brownish-pink color, which gradually becomes darker by exposure to air, until eventually a brownish precipitate of hydrated sesquioxide of cobalt is produced. But the cobalt solution, when made with ammonia containing carbonate of ammonium, or even with carbonate of ammonium itself, has a fine pink color, which is tolerably permanent. Cobalt compounds are best recognized by fusion with the borax bead, to which they impart a deep purple-blue color.

The ammoniacal solution of **manganese** is at first colorless, but by exposure to air it speedily becomes brown and opaque, from the conversion of the white soluble prothydrate into the brown insoluble sesquihydrate. Manganese compounds are very frequently contaminated with iron; hence, when excess of ammonia produces a brown precipitate, it is often worth while to pour the mixture on to a filter, and to test the ammoniacal filtrate with sulphide of ammonium;

whereupon manganese, if present, is precipitated as a flesh-colored sulphide. Manganese is best recognized before the blowpipe by fusing some carbonate of sodium, to which a little nitre may be added, upon platinum foil, and then introducing a minute portion of the manganese compound, whereby a bright green fusible mass of manganate of sodium Na_2MnO_4, is produced.

(40.) δ. The potash solution of **chromium** is of a green color, and when boiled for a longer or shorter time, according to the relative proportions of potash and chrome present, deposits the whole of its chrome in the form of a green precipitate. Chrome compounds are best recognized by the emerald green color they impart to the borax bead; and by the bright yellow mass of chromate of alkali metal which they yield when ignited on platinum foil, with carbonate of sodium and nitre, before the blowpipe.

ε. The potash solution of **zinc**, when containing a considerable excess of potash, is not affected even by prolonged ebullition; but when containing only a slight excess, it soon deposits an opaque white precipitate. On adding a few drops of *sulphide of ammonium* to potash solution of zinc, sulphide of zinc is formed, which being, unlike the hydrate of zinc, insoluble in potash, is thrown down as a white precipitate, frequently having a grayish tinge from the accidental presence of a trace of lead in the potash used as the reagent.

Zinc compounds when strongly heated leave a fixed infusible residue, which, when cold, is quite white, but when hot has a deep greenish-yellow tint. Moistened with nitrate of cobalt solution and re-ignited, it acquires a pure permanent chrome-green color.

ζ. The potash solution of **alumina** is unaffected by boiling, and also by the addition of a few drops of sulphide of ammonium, unless indeed the potash contains an appreciable quantity of lead, when a black precipitate of sulphide of lead is formed.

Ammonia or carbonate of ammonium gives a simi-

lar white precipitate with zincous and albuminous salts, but the precipitate produced with the former is freely soluble, while that produced with the latter is insoluble in excess of the reagent. Hence the addition of *chloride of ammonium* to potash solution of zinc produces no precipitate; but when added in sufficient quantity to potash solution of alumina, it throws down a white gelatinous precipitate of hydrate of aluminum, owing to a substitution of free ammonia for free potash, thus:—

$$NH_4Cl + KHO = KCl + NH_4HO, \text{ or } NH_3.H_2O.$$

Compounds of aluminum, when strongly heated in the blowpipe flame, leave a white, infusible, highly incandescent residue, which, when moistened with solution of nitrate of cobalt, and re-ignited, assumes a fine permanent blue color.

§ V.—EXAMINATION FOR BASES OF GROUP III.

(41.) This group includes the bases which are not precipitated either by sulphuretted hydrogen, or by sulphide of ammonium. A solution of the salt in water or acid may be at once examined, according to the directions of Table III. Or the solution, which has been successively treated with sulphuretted hydrogen and sulphide of ammonium without the production of a precipitate, may be tested for any of the metals of this group, except potassium, sodium, and ammonium. If the original substance required an acid to effect its solution, its base cannot be any one of the last three, inasmuch as all simple salts of potassium, sodium, and ammonium are soluble in hot water.

Table III.

(42.) Examination of a solution containing some one member of the third group of bases; namely, Barium, Strontium, Calcium, Magnesium, Potassium, Sodium, or Ammonium. The sulphides or sul-

phydrates of these metals being soluble in water, the solutions of their salts are not precipitated either by sulphuretted hydrogen, or by sulphide or sulphydrate of ammonium.

α. Add *chloride and carbonate of ammonium* to the original solution, and warm gently.

<table>
<tr><td colspan="3">Precipitated
Barium
Strontium
Calcium.

β. Add sulphate of potassium or dilute sulphuric acid to the original solution.</td><td colspan="3">Dissolved
Magnesium
Potassium
Sodium
Ammonium.

γ. Add phosphate of ammonium to the above solution already containing the ammoniacal salts, and stir.</td></tr>
<tr><td colspan="2">Precipitated
Barium (quickly)
Strontium (slowly).

Add chromate of potassium to the original solution.</td><td rowspan="2">Dissolved
Calcium.</td><td rowspan="2">Precipitated
Magnesium.</td><td colspan="2">Dissolved
Potassium
Sodium
Ammonium.

δ. Add to the orinal solution tartaric acid in excess, and stir.</td></tr>
<tr><td>Precipitated
Barium.</td><td>Dissolved
Strontium.</td><td>Precipitat'd
Potassium.</td><td>Dissolved
Sodium.
Ammonium?</td></tr>
</table>

(43.) α. *Carbonate of ammonium* produces in solutions containing **barium, strontium,** or **calcium,** a white precipitate, the carbonates of these three metals being insoluble :—

$$\overset{\prime\prime}{Ca}Cl_2 + (NH_4)_2CO_3 = 2NH_4Cl + \overset{\prime\prime}{Ca}CO_3, \text{ or } CaO.CO_2.$$

When carbonate of ammonium is added to an acid solution of the compound under examination, care must be taken to add a quantity more than sufficient

to neutralize the acid, or, in other words, enough to render the solution alkaline. Inasmuch as the carbonic gas evolved on adding carbonate of ammonium to an acid liquid retains the carbonates of the alkaline earth-metals in solution, it must be expelled by gentle warming. Carbonate of **magnesium** also is insoluble in water, though readily soluble in solutions containing chloride of ammonium or other ammoniacal salt. Hence the necessity of adding chloride as well as carbonate of ammonium to the aqueous solution of the substance under examination, in order to prevent a precipitate of carbonate of magnesium being formed, and confounded with one of the other precipitable carbonates. But when the substance has been dissolved in an acid, the carbonate of ammonium expended in neutralizing the acid forms a sufficient quantity of neutral ammoniacal salt to prevent the precipitation of carbonate of magnesium; and consequently the separate addition of chloride of ammonium is rendered unnecessary. The addition of chloride of ammonium may also be dispensed with, when the carbonate is added to a portion of the solution with which a negative result has been obtained by successive treatment with sulphuretted hydrogen and sulphide of ammonium. Carbonate of ammonium also precipitates most of the metals belonging to the first and second groups, so that it can only be depended upon to indicate the presence of the alkaline earth-metals, when absence of all other precipitable metals has been previously ascertained by sulphuretted hydrogen and sulphide of ammonium respectively.

β. Sulphate of **calcium** is very slightly soluble in water, sulphate of **strontium** still less so, and sulphate of **barium** quite insoluble. Hence sulphuric acid and most soluble sulphates give precipitates in the solution of all three metals. But owing to the sparing solubility of *sulphate of potassium* in water, its solution does not usually precipitate the salts of calcium unless very concentrated, though it is readily

capable of precipitating thosc of strontium and barium:—

$$\overset{\prime\prime}{Ba}Cl_2 + K_2SO_4 = 2KCl + \overset{\prime\prime}{Ba}SO_4, \text{ or } BaO.SO_3.$$

Moreover, a solution of sulphate of calcium will not precipitate salts of calcium under any circumstances, but will nevertheless precipitate those of strontium and barium, the former slowly, the latter immediately.

Oxalate of ammonium is the reagent usually employed to demonstrate the prescnce of **calcium,** with neutral or alkaline solutions of which it gives a white precipitate of oxalate of calcium, soluble in nitric and hydrochloric, but insoluble in acetic and óxalic acids:—

$$\overset{\prime\prime}{Ca}Cl_2 + (NH_4)_2C_2O_4 = 2NH_4Cl + \overset{\prime\prime}{Ca}C_2O_4, \text{ or } CaO.C_2O_3.$$

But oxalate of ammonium produces precisely similar precipitatcs in neutral salts of strontium and barium, the oxalates of these two metals being also insoluble in water. That of barium, however, is soluble in excess of warm oxalic acid. Moreover, free oxalic acid precipitates neutral solution of calcium and strontium, but not of barium, unless very concentratcd.

In solutions acidified with acetic acid, *chromate of potassium* has no action upon strontium and calcium salts, but throws down from barium salts a yellow precipitate of chromate of barium, soluble in the nitric and hydrochloric acids:—

$$\overset{\prime\prime}{Ba}(NO_3)_2 + K_2CrO_4 = 2KNO_3 + \overset{\prime\prime}{Ba}CrO_4.$$

Hydrofluosilicic acid also serves to distinguish **barium** salts from those of strontium and calcium, with the first of which it alone produces a precipitate, the fluosilicate of barium being alone insoluble. This test is unaffected by the presence of nitric and hydrochloric acids:—

$$\overset{\prime\prime}{Ba}Cl_2 + H_2SiF_6 = 2HCl + \overset{\prime\prime}{Ba}SiF_6, \text{ or } \overset{\prime\prime}{Ba}F_2.SiF_4.$$

Most barium salts, especially when moistened with hydrochloric acid, impart an apple-green color to the blowpipe flame; strontium salts a marked crimson; and calcium salts an orange-red.

(44) γ. *Phosphate of ammonium*, or *of sodium*, gives with **Magnesian** solutions, containing carbonate of ammonium or free ammonia, a white crystalline precipitate of phosphate of magnesium and ammonium, frequently known as triple phosphate:—

$$\overset{\prime\prime}{Mg}Cl_2 + (NH_4)_2HPO_4 + NH_3 = 2NH_4Cl + \overset{\prime\prime}{Mg}(NH_4)PO_4.$$

This precipitate does not usually form in warm solutions, and is frequently produced only after brisk stirring, or rubbing the inside of the tube with a glass rod. It must be remembered that phosphate of ammonium gives precipitates with salts of barium, strontium, and calcium, and of most metals belonging to the first and second groups, so that it can only be relied upon as a test for magnesium when the absence of all other metals precipitable by it has been first ascertained.

δ. *Tartaric acid* gives with neutral solutions of potassium salts a white crystalline precipitate of acid tartrate of potassium or cream of tartar:—

$$KCl + H_6C_4O_6 = HCl + KH_5C_4O_6.$$

The precipitate does not usually appear in a warm liquid. It is produced very slowly in solutions of the more sparingly soluble, and in dilute solutions of the more freely soluble potassium salts. From such solutions it is best obtained by cooling the mixture under a tap, diluting it with a little alcohol, and stirring it briskly with a glass rod, which should be rubbed against the inside of the tube. In testing alkaline solutions for the presence of potassium, care must be taken to add an excess of tartaric acid. The precipitate of cream of tartar is not formed in solutions of potassium salts which have a marked acid reaction from the presence either of oxalic acid, or

of one of the strong mineral acids. But on neutralizing such solutions with caustic soda, or carbonate of sodium, and then adding tartaric acid, the characteristic precipitate is readily obtained.

Perchloride of platinum produces also in solutions of **potassium**-salts, which should first be acidulated with hydrochloric acid, a yellow crystalline precipitate of platino-chloride of potassium $2KCl.PtCl_4$, the deposition of which is facilitated by stirring, and by the addition of alcohol.

Solutions of **ammonium**-salts, when moderately concentrated, resemble potassium-salts in their behavior with tartaric acid, yielding therewith a crystalline precipitate of acid tartrate of ammonium $(NH_4)H_5C_4O_6$. Hence ammonia cannot be used to neutralize those acid solutions which have to be tested with tartaric acid for the presence of potassium. Moreover, moderately concentrated solutions of ammonium-salts give with dichloride of platinum a yellow crystalline precipitate of platino-chloride of ammonium $2NH_4Cl.PtCl_4$, resembling the similar compound of potassium. Dilute solutions of ammoniacal salts behave like solutions of **sodium**-salts in not furnishing any precipitate with either tartaric acid or dichloride of platinum. But ammonium-salts may be readily distinguished from those of potassium and sodium by their partial or complete volatility, and by their solutions evolving ammonia when boiled with potash or lime:—

$$NH_4Cl + KHO = KCl + NH_3 + H_2O.$$

Sodium-salts impart an intense yellow coloration to flame, and **potassium**-salts a marked violet.

§ VI.—EXAMINATION FOR ACIDS.

(45.) The student should always ascertain the nature of the metallic or basic constituent of his substance, before proceeding to search for its acid or chloroid constituent. In this search he will be

greatly assisted by a knowledge of the special characters of particular salts, and of the general characters of various classes of salts. Knowing, for instance, that sulphate of barium is insoluble in all menstrua, he need not test a soluble barium salt for sulphuric acid. On the other hand, a salt insoluble in water is not likely to be a nitrate or chlorate. The following classes of salts are, as a rule, soluble in water: Nitrates, excepting a few superbasic salts; acetates, except acetate of silver, which is only sparingly soluble; chlorides, except chloride of silver, which is insoluble in boiling nitric acid, and mercurous chloride, or calomel, which dissolves in boiling nitric acid with conversion into mercuric salt: chloride of lead is moderately soluble in boiling, though very sparingly soluble in cold water. Sulphates, except those of barium, strontium, and lead, which last is soluble in boiling hydrochloric acid: the sulphates of silver and calcium also are only sparingly soluble. The following classes of salts are, as a rule, insoluble in water: Oxides or hydrates, and sulphides or sulphydrates, except those of the alkali- and alkaline earth- metals, and the sulphydrate of magnesium; also carbonates, phosphates, and oxalates in general, except those of the alkali metals, and many hyperacid salts.

The presence of any particular acid is indicated more or less certainly by the behavior of the substance when gently heated in the solid state with three or four times its bulk of strong *sulphuric acid*, and when under examination for the detection of its metallic constituent.

The most usual decomposition which takes place between sulphuric acid and the salt of a more volatile or feeble acid consists in an exchange of the hydrogen of the sulphuric acid for the metal of the salt, thus:—

$$H_2SO_4 + NaCl = NaHSO_4 + HCl$$
$$H_2SO_4 + KNO_3 = KHSO_4 + HNO_3.$$

Reactions similar to the above take place with the salts of nearly all acids, provided the sulphuric acid

employed is not too strong, and the heat not too great; but with ordinary oil of vitriol, especially at a somewhat high temperature, the liberated acids themselves often undergo a partial or complete decomposition.

The tartaric and citric acids, for instance, are destroyed with more or less charring. The nitric and chloric acids yield the peroxides of nitrogen and of chlorine respectively, thus:—

$$2HNO_3 = H_2O + N_2O_4 + O$$
$$2HClO_3 = H_2O + Cl_2O_4 + O$$

except that, in the former case, the decomposition is but slight, while in the latter, the separated oxygen converts another portion of the chloric into perchloric acid.

Oxalic acid breaks up into water, carbonous oxide, and carbonic anhydride, thus:—

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

The hydrobromic, hydroiodic, and sulphydric acids are decomposed with liberation of bromine, iodine, and sulphur, respectively, thus:—

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$$
$$2HI + H_2SO_4 = 2H_2O + SO_2 + I_2$$
$$H_2S + H_2SO_4 = 2H_2O + SO_2 + S$$

Hydrocyanic acid yields acid-sulphate of ammonia and carbonous oxide, thus:—

$$HCN + H_2O + H_2SO_4 = CO + NH_3.H_2SO_4.$$

(46.) In the following table the principal acids are classified according to the behavior of their salts when under examination for bases, and when warmed with strong sulphuric acid:—

TABLE IV.—PRELIMINARY TESTING FOR ACIDS.

α. Indicated during previous examination.	β. Corporated by sulphuric acid.	γ. Also react with sulphuric acid.	δ. No obvious effect with sulphuric acid
ARSENATES CHROMATES } React with H_2S	NITRATES. Brown acid vapors with copper	CHLORIDES. Pungent acid fumes. With MnO_2 evolve chlorine	BORATES. Give green flame with alcohol
NITRATES CHLORATES } Deflagrate	CHLORATES. Browning and crackling detonation.	BROMIDES. Brown fumes, which bleach litmus, and turn starch yellow	OXALATES CYANIDES } Effervesce?
TARTRATES CITRATES } Char	TARTRATES CITRATES } Char	IODIDES. Violet vapors, which turn starch paper purple	PHOSPHATES ARSENATES SULPHATES SILICATES OXIDES
CARBONATES SULPHIDES SULPHITES, &c. PEROXIDES } Effervesce with HCl	CARBONATES SULPHIDES SULPHITES } Effervesce	FLUORIDES. Pungent acid fumes, which etch glass	
PERSULPHIDES SILICATES BORATES BENZOATES } Give precipitates with HCl		ACETATES. Acid vapor With alcohol yield acetic ether	

(47.) *a.* Deflagration of the substance, when heated upon charcoal before the blowpipe, shows the probable presence of a **nitrate** or **chlorate.**

Charring of the substance, when heated upon platinum foil or charcoal, usually indicates the presence of a **tartrate** or **citrate.**

Effervescence from the substance, when its solution is being effected in hydrochloric acid, occurs with several classes of salts.

With nearly all **carbonates** there is evolution of carbonic anhydride, thus:—

$$2HCl + \overset{''}{Ca}CO_3 = \overset{''}{Ca}Cl_2 + H_2O + CO_2.$$

The gas is free from any marked smell, and renders lime-water milky (vide par. 84).

With many **sulphides** there is evolution of sulphydric acid or sulphuretted hydrogen, thus:—

$$2HCl + \overset{''}{Fe}S = \overset{''}{Fe}Cl_2 + H_2S$$
$$6HCl + \overset{'''}{Sb}_2S_3 = 2\overset{'''}{Sb}Cl_3 + 3H_2S.$$

The gas smells most offensively, and turns lead paper of a black or brown color.

With **sulphites** and **hyposulphites** (*vide* par. 94) there is evolution of sulphurous anhydride, thus:—

$$2HCl + Na_2SO_3 = 2NaCl + H_2O = SO_2.$$

The gas has the peculiar suffocating smell of burning sulphur, and produces a purple discoloration on starch paper moistened with iodic acid solution.

With **peroxides** there is evolution of chlorine, thus:—

$$4HCl + MnO_2 = 2H_2O + \overset{''}{Mn}Cl_2 + Cl_2.$$

The gas, which has a greenish color and characteristic irritating smell, produces a purple coloration on starch paper moistened with iodide of potassium.

Similar effects are observable on acidifying with hydrochloric acid the strong aqueous solutions of soluble carbonates, sulphides or sulphydrates, sulphites, and hyposulphites; but the evolution of chlorine under these circumstances would probably be due to the presence of a hypochlorite. Moreover, most simple **cyanides**, and the strong aqueous solutions of such of them as are soluble, effervesce when warmed with hydrochloric acid, from an evolution of hydrocyanic acid gas, known by its characteristic smell, and by its behavior with sulphide of ammonium, &c. (*vide* par. 99).

$$HCl + KCN = KCl + HCN.$$

The aqueous solutions of certain salts when acidified with hydrochloric acid yield precipitates due, not to the metals silver, lead, and mercury, but to the acids of the respective salts.

With **persulphides** there is formed a yellowish white turbidity from liberated sulphur, always accom-

panied, however, by an evolution of sulphuretted hydrogen:—

$$2HCl + K_2S_2 = 2KCl + H_2S + S.$$

With hyposulphites, there is gradually produced a more decidedly yellow precipitate of sulphur, and an evolution of sulphurous anhydride, thus:—

$$2HCl + Na_2S_2O_3 = 2NaCl + H_2O + SO_2 + S.$$

With soluble **silicates** there is produced a gelatinous precipitate of silica, which separates out more completely, and becomes gritty on evaporation:—

$$2HCl + K_2SiO_3 = 2KCl + H_2O + SiO_2.$$

Borates, and **benzoates**, if sufficiently concentrated, yield crystalline precipitates of boric and benzoic acids respectively, which dissolve in boiling water, and crystallize out again on cooling:—

$$HCl + NaH_5(BO_3)_2 = NaCl + 2H_3BO_3.$$
$$HCl + KH_5C_7O_2 = KCl + H_6C_7O_2.$$

In testing for bases of the first group, by treating the acidified solution of the substance with sulphuretted hydrogen, strong evidence of the presence of arsenates or chromates may also be afforded. Acidified solutions of **arsenates** slowly yield a yellow precipitate of mixed trisulphide of arsenic and sulphur, thus:—

$$5H_2S + 2HCl + 2KH_2AsO_4 = 8H_2O + 2KCl + As_2S_3 + S_2.$$

Acidified solutions of **chromates** yield a yellowish-white deposit of sulphur, while the color of the liquid changes from orange-red to green, owing to the reduction of the chromic acid to the state of a chrome-salt, thus:—

$$3H_2S + 6HCl + 2Cr''O_3 = 6H_2O + 2CrCl_3 + S_3.$$

(48.) β. **Nitrates**, when heated with sulphuric acid, give off nitric acid vapors, sometimes having a brownish tint from the presence of peroxide of nitro-

gen. On the addition of a few copper turnings the brown color becomes very marked, from the evolution of colorless nitric oxide N_2O_2, and its immediate conversion into brown peroxide of nitrogen N_2O_4, by an absorption of atmospheric oxygen:—

$$3H_2SO_4 + 3Cu + 2HNO_3 = 3\overset{\prime\prime}{Cu}SO_4 + 4H_2O + N_2O_2.$$

The vapor, whether before or after the addition of copper, has a characteristic nitrous smell, reddens litmus paper, and gives a purple coloration to starch paper moistened with iodide of potassium:—

$$2KI + N_2O_4 = 2KNO_2 + I_2.$$

Chlorates react somewhat violently with sulphuric acid, producing an immediate browning, and, either at once or on the slightest application of heat, a crackling, or even loud detonation, from the breaking up of the peroxide of chlorine first liberated.

Tartrates and citrates undergo more or less charring, the tartrates becoming thoroughly blackened, the citrates merely browned.

Carbonates, sulphites, and sulphides effervesce with sulphuric as with hydrochloric acid; except that in the last case some of the liberated sulphydric acid reacts with the excess of sulphuric acid to form sulphur, water, and sulphurous anhydride, as already described (*vide* par. 45).

γ. Most **chlorides** when warmed with sulphuric acid evolve hydrochloric acid gas, which reddens litmus paper, and has a well characterized pungent smell. On the addition of a little peroxide of manganese, chlorine is evolved, recognizable by its peculiar irritant smell:—

$$H_2SO_4 + MnO_2 + 2HCl = \overset{\prime\prime}{Mn}SO_4 + 2H_2O + Cl_2.$$

It bleaches litmus, and produces a purpling of starch paper moistened with iodide of potassium solution.

Bromides evolve a mixture of hydrobromic acid with bromine vapor, the latter recognizable by its

brown color, irritant smell, and power of bleaching litmus.

Iodides yield iodine vapor, recognizable by its violet color, and by its rendering starch paper purple.

Fluorides give off pungent fumes of hydrofluoric acid, which redden litmus and etch glass (*vide* par. 106).

Acetates give off acetic acid vapors, which redden litmus. On the addition of a little alcohol the original sour smell of the acid is changed into the fruity smell of acetic ether.

δ. **Borates** do not react visibly with sulphuric acid, but on adding alcohol, and then setting fire to the mixture in a capsule, the flame presents a marked green color.

Oxalates and **cyanides** are decomposed by heated sulphuric acid with liberation of carbonous oxide gas, accompanied in the case of the former salts with carbonic anhydride; but as the evolution of gas is liable to be overlooked, and the gas itself does not present any striking property, the oxalates and cyanides are here included among the salts with which sulphuric acid produces no obvious effect.

Phosphates, arsenates, sulphates, silicates, and **oxides** do not react visibly with sulphuric acid; except that with some peroxides there is evolution of oxygen, transformable into that of chlorine on the addition of chloride of sodium or hydrochloric acid.

(49.) The various liquid tests for the acids should be applied by preference to an aqueous solution of the original substance. But if insoluble in water, and consequently neither a nitrate nor a chloride, it may be dissolved in dilute nitric or hydrochloric acid, and the tests applied to the solution so formed.

The presence of certain basic metals interferes occasionally with the described reactions of several of the acids. Thus solution of hydrochloric acid or any chloride, when tested with nitrate of silver, gives a white precipitate of chloride of silver, said to be readily soluble in ammonia. But on adding nitrate

of silver to solution of mercuric chloride, and treating the resultant white precipitate with ammonia, there is no obvious solution produced, because, although the precipitated chloride of silver does actually and completely dissolve, a white insoluble mercurammonium compound is simultaneously thrown down from the mutual reaction of the ammonia and mercuric salt.

Bearing in mind, however, the interference likely to be produced by the presence of the particular metal previously detected, the tests for sulphuric, hydrochloric, and nitric acids can for the most part be satisfactorily applied to any of their salts.

But in testing for phosphoric, oxalic, and tartaric acids more particularly, and for other acids when any difficulty occurs, it is important that the base of the salt should be one of the alkali metals, potassium, or sodium, or ammonium.

The bases of the first group may be got rid of by saturating the solution with sulphuretted hydrogen gas, filtering, evaporating the filtrate until it ceases to smell, and neutralizing it with carbonate of sodium or potassium.

The bases of the second group, together with barium, strontium, calcium, and magnesium, may be removed by adding to the acidulous, or occasionally to the aqueous, solution of the substance an excess of carbonate of sodium or potassium, boiling for some time, and filtering. The filtrate can afterwards be neutralized with nitric or hydrochloric acid, which may be conveniently added drop by drop from a pipette.

(50.) The following abridged table shows the action of some general reagents upon the dissolved salts of the principal acids. By its aid and that of the preceding table, the student will rarely have much difficulty in quickly discovering the acid constituent of his substance, although, indeed, the course of examination is not so systematic as that for the bases. A more complete table for the detection of the acids

would include the reactions of a few organic salts of comparatively rare occurrence, such as the formates, succinates, citrates, meconates, gallates, tannates, and ferrid-cyanides; of a few mineral salts of similarly rare occurrence, namely, the iodates, seleniates, and silico-fluorides; of a few mineral salts rarely met with in the soluble form, namely, silicates and fluorides; and of the previously detected arsenates. It would also mention the several precipitates given by nitrate of silver and nitrate of barium respectively, which disappear on acidification, and have, as a rule, but little practical interest.

TABLE V.—COURSE FOR DETECTION OF THE ACIDS.

α. Nitrate of silver.	β. Nitrate of Barium.	γ. Chloride of Calcium.	ε. Perchloride of Iron.
From acid solutions	From acid solutions	From acetic acid solutions	From acid solutions
CHLORIDES CYANIDES } White BROMIDES	SULPHATES. White	OXALATES. White	FERROCYANIDES. D. blue pp. SULPHOCYANIDES. D. red color
IODIDES. Yellow	From non-acid solutions	From neutral sols.	
SULPHIDES. Black	CHROMATES. Yellow CARBONATES SULPHITES } White &c. &c.	TARTRATES. White	From neutral sols. BORATES BENZOATES } L. brown pp. ACETATES. D. red color.
		δ. SULPHATE OF MAGNESIUM From ammon. sols. PHOSPHATES. White	

(51.) a. *Nitrate of silver* causes precipitates in the solutions of very many classes of salts, the majority of silver salts being more or less insoluble in water. The reactions consist in an exchange of the silver of the nitrate of silver for the metal or quasi-metal of the dissolved salt under examination, as illustrated by the following examples:—

$$\begin{array}{llllll} AgNO_3 & + & KI & = & KNO_3 & + \ AgI \\ 3AgNO_3 & + & FeCl_3 & = & Fe(NO_3)_3 & + \ 3AgCl \\ 2AgNO_3 & + & (NH_4)_2C_2O_4 & = & 2NH_4NO_3 & + \ Ag_2C_2O_4 \\ 3AgNO_3 & + & Na_2HPO_4 & = & \left\{\begin{array}{l} 2NaNO_3 \\ HNO_3 \end{array}\right. & + \ Ag_3PO_4 \end{array}$$

All the precipitates produced by nitrate of silver disappear upon the addition of nitric acid, or do not form in presence of free nitric acid, except the chloride, cyanide, bromide, iodide, and sulphide.

With **chlorides** the silver precipitate is white, becoming slate-colored on exposure to light, and soluble in ammonia before discoloration. Upon heating the original substance with peroxide of manganese and sulphuric acid, chlorine gas is evolved.

With simple* **cyanides** the silver precipitate is white, soluble in ammonia, and in boiling concentrated nitric acid: a portion of the precipitate washed by decantation may be treated with yellow sulphide of ammonium, whereby sulphide of silver and sulphocyanate of ammonium are produced, which last strikes a deep red color on the addition of a ferric salt. An excess of sulphide of ammonium must be avoided, or afterwards got rid of by evaporation to dryness.

With **bromides** the silver precipitate is white, and with difficulty soluble in ammonia. Bromine is liberated from the original salt, when treated with sulphuric acid, and from the solution of the salt when treated with a few drops of nitro-hydrochloric acid or chlorine-water, whereby the liquid assumes a red-brown color rendered more evident upon the addition of a little ether or chloroform, which dissolves out the bromine to form a deep brown stratum.

With **iodides** the silver precipitate has a pale yellow color, and is insoluble in, but turned white by, ammonia. Iodine is liberated from the salt when treated with sulphuric acid, and from the solution of the salt when treated with a few drops of yellow nitric or nitro-hydrochloric acid or chlorine-water, its presence being manifested by the purple color it

* Ferrocyanide and sulphocyanate of silver occur as white precipitates, and the ferridcyanide as a brown precipitate, all unaffected by nitric acid, but soluble ferrocyanides, ferridcyanides, and sulphocyanates are recognized immediately by their behavior with iron solutions.

produces on starched paper, or with dilute starch paste added to the liquid, or by the pink or crimson color it imparts to chloroform.

With **sulphides** the silver precipitate is black, and insoluble in ammonia, but soluble in boiling nitric acid. Nitro-prusside of sodium added to an alkaline sulphide produces a deep purple coloration.

Of the silver precipitates which disappear on acidification with nitric acid, the hydrate is brown, the chromate dark red, the arsenate brick-red, the phosphate bright yellow, though sometimes white, the carbonate pale yellow, and the rest white. The oxalate is insoluble in acetic acid; the acetate is thrown down from concentrated solutions only; the tartrates, formates, and sulphites are reduced to the metallic state on boiling; while the borates, benzoates, and citrates do not exhibit any characteristic property.

(52.) β. *Nitrate* or *chloride of barium* precipitates the solutions of many classes of salts, most barium salts being insoluble or sparingly soluble in water. The reaction consists in an exchange of the barium of the nitrate or chloride of barium for the metal or quasi-metal of the salt under examination, thus:—

$$\overset{''}{Ba}(NO_3)_2 + Na_2SO_4 = 2NaNO_3 + \overset{''}{Ba}SO_4$$

$$\overset{''}{Ba}Cl_2 + KHSO_4 = KCl + HCl + \overset{''}{Ba}SO_4$$

With **sulphates** the barium precipitate is white, and, if in any quantity, opaque. It does not disappear upon the addition of nitric or hydrochloric acid, but is nevertheless slightly soluble in concentrated nitric acid. The seleniate and silicofluoride of barium also occur as white precipitates unaffected by acidification (*vide* par. 95). Of the barium precipitates which dissolve in nitric or hydrochloric acid, the chromate is yellow and the remainder are white. The carbonate and sulphite dissolve with effervescence. The arsenate, borate, and tartrate do not form in the presence of ammoniacal solutions, and, when once thrown down, disappear more or less readily on the

addition of chloride of ammonium. The oxalate and phosphate exhibit no characteristic properties.

(53.) γ. With a few exceptions, *chloride of calcium* causes precipitates with the several classes of salts which are precipitated by chloride or nitrate of barium; but while sulphate of barium is much more insoluble in water and acids than sulphate of calcium, oxalate of calcium is more insoluble in water, and especially in acetic acid, than oxalate of barium.

With solutions of **oxalates** in which there is no free mineral acid, chloride or sulphate of calcium produces an opaque white precipitate of oxalate of calcium, the deposition of which, when in small quantity, may be facilitated by stirring:—

$$\overset{''}{Ca}Cl_2 + K_2C_2O_4 = 2KCl + \overset{''}{Ca}C_2O_4.$$

The precipitate is insoluble in ammonia and in acetic acid, but soluble in dilute nitric or hydrochloric acid. Its solubility in mineral acids distinguishes it from sulphate of calcium, which is occasionally thrown down by chloride of calcium from strong solutions of sulphates, as does also its property of effervescing with sulphuric acid and peroxide of manganese; while its insolubility in acetic acid distinguishes it from the phosphate, tartrate, carbonate, and other salts of calcium insoluble in water.

The solution to be tested for oxalic acid with chloride of calcium may be alkaline, or neutral, or acid from acetic acid only. If an alkaline carbonate is present from its employment in preparing the solution, it should be neutralized with acetic or hydrochloric acid. If an excess of mineral acid is present, it may either be neutralized with ammonia, or acetate of ammonia may be added, whereby the free mineral acid is replaced by free acetic acid, thus:—

$$HCl + (NH_4)H_3C_2O_2 = NH_4Cl + H_4C_2O_2;$$

but in practice it is better to add the ammonia and acetic acid separately.

In neutral solutions of **tartrates,** chloride of cal-

cium gives a white precipitate of tartrate of calcium, soluble even in acetic acid:—

$$\overset{\prime\prime}{Ca}Cl_2 + KNaH_4C_4O_6 = KCl + NaCl + \overset{\prime\prime}{Ca}H_4C_4O_6.$$

On digesting the precipitate with potash, filtering, and boiling the filtrate, a white turbidity is produced, which disappears on cooling. This behavior with potash distinguishes the tartrate from the phosphate and other insoluble salts of calcium. Tartrate of calcium is not thrown down in the presence of much ammoniacal salt.

(54.) δ. Although phosphate solutions are precipitated alike by nitrate of silver, nitrate of barium, chloride of calcium, sulphate of magnesium, and perchloride of iron, it is the magnesian precipitate more especially which is characteristic of phosphoric acid. From a neutral or alkaline **phosphate** solution, a mixture of *sulphate of magnesium*, chloride of ammonium and ammonia throws down a white crystalline precipitate of phosphate of ammonium and magnesium, thus:—

$$\overset{\prime\prime}{Mg}SO_4 + NH_3 + Na_2HPO_4 = Na_2SO_4 + NH_4\overset{\prime\prime}{Mg}PO_4.$$

In common with all magnesian precipitates, it is readily soluble in acids; but, unlike any other magnesian salt, except the arsenate, it is insoluble in ammonia and ammoniacal salts. The yellow precipitate given with nitrate of silver is a useful confirmatory test, as is also the reaction with molybdate of ammonium (*vide* par. 100), although this last is common to the phosphoric and arsenic acids.

(55.) ε. *Perchloride of iron*, which, for most purposes, should be free from any excess of acid, causes precipitates or characteristic alterations of color in the solutions of very many classes of salts, among which may be mentioned the following:—

With **ferrocyanides** a dark blue precipitate of Prussian blue, Fe_7Cy_{18} or $3Fe''Cy_2.4Fe'''Cy_3$, is thrown down; while with **sulphocyanates** a dark-red color,

due to ferric sulphocyanate $Fe'''(CyS)_3$, is developed, neither of which results is affected by the addition of hydrochloric acid. With neutral **borates**, **benzoates**, or **phosphates**, there is produced a pale brown precipitate of borate, benzoate, or phosphate of iron, which disappears on the addition of hydrochloric acid. The phosphate, however, $Fe'''PO_4$, is scarcely affected by acetic acid, save in presence of a large excess of iron.

With neutral **acetates** and **sulphites**, there is produced a dark reddish-brown coloration, which disappears on the addition of hydrochloric acid, or on boiling: in the latter case with formation of a red-brown turbidity.

Nitrates and **chlorates** are unaffected by any of the general reagents mentioned in the table.

(56.) Although nearly all of the acids react more or less characteristically with several reagents as above described, the following list of acids or salts, with the tests by which their presence is more particularly indicated or established, may prove useful to the student:—

CHROMATES	Reaction with sulphydric acid.
NITRATES CHLORATES	Deflagration on charcoal, and reaction with sulphuric acid.
CARBONATES SULPHIDES SULPHITES	Effervescence with acids.
SULPHATES	Precipitation by chloride of barium.
CHLORIDES BROMIDES IODIDES CYANIDES	Precipitation by nitrate of silver.
PHOSPHATES	Precipitation by sulphate of magnesium.
OXALATES TARTRATES	Precipitation by chloride of calcium.
ACETATES BENZOATES	Reaction with perchloride of iron.
BORATES FLUORIDES SILICATES	Special tests.

In the paragraphs, 89 to 107, describing the several reactions of the individual acids, the order of the above list is adopted.

§ VII.—SPECIAL SUBSTANCES.

(57.) It being scarcely possible to give general rules that shall apply to every particular case, there yet remain for consideration certain compounds, the detection of which according to the directions of the preceding tables is impracticable, or difficult, or liable to fallacy. There are some few substances, for instance, which are insoluble in all ordinary menstrua, and which must consequently be submitted to special modes of treatment, so that they may be transformed into new and soluble combinations. Again, there are those compounds of barium, strontium, calcium and magnesium, which are precipitated by sulphide of ammonium along with the members of the second group, and which are known by the laboratory-name of earthy salts. There are also the oxides, or compounds without an acid, and the acids or compounds without a base other than hydrogen, together with two or three miscellaneous bodies. A few remarks, moreover, are appended on the examination of substances in the dissolved or liquid condition, and on the solubility of the heavy metals in alkaline solutions.

(58.) Insoluble Compounds.

Many substances are known which do not dissolve in water or in any ordinary acid, or in any combination of acids, even with the aid of heat. Among bodies of this class, the following are most likely to come under the notice of the student: namely, peroxide of tin; peroxide of antimony; chloride, bromide, and iodide of silver; the sulphates of barium, strontium, and perhaps lead; chromic oxide; alumina and some aluminates; with silica and some silicates.

Several of these bodies may be met with in the soluble as well as the insoluble form, but the silver compounds and earthy sulphates are always alike insoluble. Sulphate of strontium, however, though practically insoluble, dissolves sufficiently in water to form a solution in which the presence of sulphuric acid can be detected by the addition of a barium-salt. Again, sulphate of lead dissolves, though not very readily or to any great extent, in boiling hydrochloric acid, forming a solution from which chloride of lead crystallizes out on cooling. For analytical purposes these more or less insoluble bodies may be classified into compounds of heavy metals easily recognizable before the blowpipe (α), and earthy compounds for whose satisfactory identification a further examination is required (β).

α. The insoluble compounds of **tin, antimony, silver,** and **lead,** when mixed with cyanide flux and heated on charcoal before the blowpipe, yield beads of metal distinguishable from one another by their appearance, texture, behavior with acids, and freedom from, or association with, incrustations of definite character (*vide* par. 26, δ). The sulphuric acid of the insoluble lead compound may be recognized by boiling it with a solution of carbonate of sodium or of potassium, filtering, and testing the clear filtrate, with nitric acid and nitrate of barium, for the presence of any alkaline sulphate resulting from the decomposition of the original sulphate of lead, thus:—

$$\overset{\prime\prime}{Pb}SO_4 + Na_2CO_3 = Na_2SO_4 + \overset{\prime\prime}{Pb}CO_3.$$

The chlorine, bromine, or iodine of the insoluble silver compound may be detected by fusing the compound with a mixture of the carbonates of sodium and potassium in a small porcelain capsule or iron spoon, and treating the resulting saline mass with sulphuric acid and peroxide of manganese, or the solution of the mass with nitric acid and nitrate of silver. By fusing the chloride, bromide, or iodide of

silver with carbonated alkali, the halogen is transferred from the silver to the alkali metal, thus:—

$$2AgCl + Na_2CO_3 = 2NaCl + Ag_2 + CO_2 + O.$$

Chromic oxide is known by its dull green color, by the bright green color it imparts to the borax bead, and by the yellow mass of alkaline chromate into which it is converted by fusion with a little nitre and carbonate of sodium. This mass may be dissolved in water, and to the yellow solution so formed the ordinary tests for chromic acid applied.

β. The remaining insoluble and non-reducible compounds may be recognized by the following process. The substance in the state of a very fine powder, and mixed with three or four times its weight of the carbonates of sodium and potassium, is fused for some time on a platinum capsule or on platinum foil, whereby a decomposition of the kind represented below is effected:—

$$\overset{''}{Ba}SO_4 + Na_2CO_3 = Na_2SO_4 + \overset{''}{Ba}CO_3$$

$$\overset{'''}{Al}_2(SiO_3)_3 + 3Na_2CO_3 = 3Na_2SiO_3 + \overset{'''}{Al}_2O_3 + 3CO_2.$$

By boiling the fused mass in water and filtering, a clear solution is obtained containing a sulphate or silicate, and perhaps some aluminate of sodium; while an undissolved residue is left upon the filter consisting of alumina, or of carbonate of barium or strontium, or possibly of the carbonate or oxide of some other basylous metal, originally existing in the form of a silicate or aluminate. This residue, after being washed with water, is dissolved in dilute hydrochloric acid, and the resulting solution tested by the usual reagents, for aluminum, barium, strontium, and the basylous metals generally.

The clear filtrate is acidified with hydrochloric acid, and a portion of it, refiltered if necessary from any deposit caused by the acidification, tested for sulphuric acid by means of nitrate or chloride of barium. The remainder, whether or not turbid from the acidi-

fication, must be evaporated to dryness, gently heated, and again acted upon with hydrochloric acid and water. Any undissolved gritty residue will consist of silica, which may be further identified by fusion with a bead of carbonate of sodium before the blowpipe; while any alumina contained in the hydrochloric acid solution will be thrown down on neutralization with ammonia.

(59.) Earthy Salts.

These compounds being insoluble in water are precipitated unchanged from their acidulous solutions upon the addition thereto of any alkaline hydrate, carbonate, or sulphide; whence their occurrence among members of the second group of bases. Perphosphate of iron, which resembles the earthy salts in the behavior of its acidulous solution with alkaline hydrates and carbonates, may be conveniently associated with them, thus:—

α.	Iron	Phosphate
β.	Barium, Strontium, Calcium	Phosphate, Oxalate, Fluoride
γ.	Magnesium	Phosphate

The identification of the different compounds when separated from one another is easily effected by the under-mentioned methods; while the more difficult process for the detection of iron, calcium, magnesium, and phosphoric acid in presence of one another is described in Chapter IV.

α. In the original acid solution, **iron** may be detected by sulphocianate or ferridcyanide of potassium; and **phosphoric** acid by molybdate of ammonium and nitric acid. After any excess of mineral acid, more than sufficient to keep the substance in solution, has been neutralized with ammonia, the addition of the acetate of ammonium produces a buff-colored precipitate of phosphate of iron, unless, indeed, the ratio of phosphoric acid to iron is very small.

β. **Barium** and **strontium** may be detected in the original solution by means of sulphate of potassium, and be distinguished by the different behavior of their salts, with hydrofluosilicic acid, or before the blowpipe. **Calcium** may also be detected in the original solution by the addition thereto of sulphate of potassium and proof spirit. The precipitated sulphate of calcium may be collected on a filter, washed with proof spirit, dissolved in water, and the resulting solution tested with oxalate of ammonium.

Phosphoric acid may be detected in the original solution by molybdate of ammonium and nitric acid.

Oxalic acid is recognizable by the effervescence produced on adding dilute sulphuric acid and peroxide of manganese to the original substance. Or it may be detected by boiling the original acid solution with excess of carbonate of sodium, filtering, rendering the filtrate slightly acid with acetic acid, and then adding chloride of calcium, when a white precipitate of oxalate of calcium will be produced. Moreover, like phosphate of iron, oxalate of calcium is thrown down from its original solution in hydrochloric acid by addition of acetate of ammonium.

Fluorine may be detected by treating the original substance with sulphuric acid and silica (*vide* par. 106).

γ. **Magnesium** in any form is not precipitated from acid solutions by sulphate of potassium and proof spirit, or by acetate of ammonia; but, in presence of **phosphoric** acid, is thrown down from its acid solution by excess of ammonia as a white crystalline deposit of triple phosphate, which may be examined microscopically, and if necessary be dissolved in acetic or hydrochloric acid, so as to form a solution that may be submitted to further examination.

(60.) Oxides and Sulphides.

The **oxides** are generally recognized by their physical properties, and by their not answering to the tests for any of the acids. Peroxides when boiled

with hydrochloric acid, or with sulphuric acid and common salt, give off chlorine gas. The soluble hydrates or hydrated oxides are known by their alkalinity to test paper; by their effervescing not at all, or but very slightly, upon the addition of an acid; and by their giving a brown precipitate with solution of the nitrate of silver. The solution of a hydrate is, moreover, distinguishable from that of a carbonate by the circumstance that an admixture with it of excess of chloride of barium does not affect its alkaline reaction.

Such of the **sulphides** as are soluble only in nitro-hydrochloric, or in concentrated nitric acid, become by the action of the acid converted into sulphates. That the sulphuric acid did not, however, exist in the original substance, is shown by fusing this latter with carbonate of sodium, when the fused mass will afford the reactions of a soluble sulphide instead of those of a soluble sulphate. Some sulphides are extremely difficult to dissolve completely in acid, in consequence of the deposition of sulphur, which fuses round the unaltered substance, and prevents any action of the acid upon it. This is particularly the case with the sulphides of arsenic and mercury in their ordinary sublimed state. But these sulphides are easily recognized by their color, their volatility, and by their reducibility with conversion into sublimed metal, when heated with soda flux, for instance.

(61.) Acids or Salts of Hydrogen.

The ordinary solid acids are known by their solubility in cold or hot water to form strongly acid liquids, which effervesce with alkaline carbonates, are not precipitated by the several reagents for the metals, and do not evolve ammonia when heated with caustic potash. The boric and phosphoric acids yield, upon ignition, fusible residues of boric anhydride, and metaphosphoric acid respectively.

The oxalic, benzoic, tartaric, and citric acids are

entirely dissipated by a prolonged heat, the two last furnishing an intermediate product of carbon.

The liquid acids, namely, the sulphuric, nitric, hydrochloric, and acetic acids, are known by their liquidity, volatility, strongly-marked acid reaction, and, except the sulphuric, by their characteristic odors. They give only negative results when tested for bases. The sulphuric and nitric acids are easily recognized by their respective actions on metallic copper, and hydrochloric acid by its action on peroxide of manganese (*vide* Chapter III.).

Acid salts, such, for instance, as the acid sulphates, oxalates, and tartrates of alkali-metal or ammonium, manifest a strongly acid reaction to test-paper, and effervesce with alkaline carbonates. But they either evolve ammonia when treated with caustic potash, or leave a fixed residue upon ignition, which, in the case of the acid oxalates and tartrates, consists of alkaline carbonate. The acid salts of potassium react with perchloride of platinum, but not with tartaric acid, unless previously neutralized with soda.

(62.) Miscellaneous Salts.

Iodide of potassium solution reacts satisfactorily when treated with tartaric acid, but yields a dark brown liquid with perchloride of platinum. But after its iodine has been precipitated with excess of nitrate of silver, and the excess of silver with hydrochloric acid, the filtered liquid yields with perchloride of platinum the characteristic yellow precipitate of potassio-chloride of platinum.

Calomel occurs as a heavy, white, volatile powder. It is readily soluble in concentrated nitric acid, but in the act of solution becomes converted into a mercuric salt. That it was originally a mercurous salt is shown by the powder itself becoming black when agitated with potash-water.

White precipitate, amido-chloride of mercury, or chloride of mercurammonium, is a mercuric com-

pound, readily distinguishable from calomel by heating it gently with potash-water, whereby it becomes of an orange-yellow color, while ammoniacal vapors are given off. It is insoluble in water, soluble in nitric and hydrochloric acids, and dissipated by heat.

The **sulphides of arsenic**, known as realgar and orpiment, are orange or yellow colored volatile solids. When boiled with nitro-hydrochloric acid, they are converted in great measure into arsenic acid, which may be obtained solid on evaporation. Its solution is precipitated very slowly by sulphuretted hydrogen, unless previously reduced by treatment with sulphurous acid.

(63.) Liquid or Dissolved Substances.

A few drops of the liquid are evaporated on a glass slip, and the residue, if any, examined microscopically. Should there be an appreciable solid residue, a further quantity of liquid may be evaporated down in a capsule, the vapor examined for its odor and reaction, and the residue submitted to ignition, &c., as described in pars. 25 and 26.

The reaction of the liquid to test-paper is next ascertained. Among volatile liquids, water, alcohol, and ether are neutral; ammonia, alkaline; and the sulphuric, nitric, hydrochloric, and acetic acids, strongly acid. These several liquids are readily distinguishable from one another by a few simple tests.

Solutions which leave a saline residue on evaporation, and are perfectly neutral, will most probably prove to contain some salt of an alkali- or alkaline earth-metal; salts of the heavy metals, with a few exceptions only, exhibiting a more or less marked acidity.

Solutions which have an alkaline reaction, known by their turning rose paper green, turmeric paper brown, or reddened litmus paper blue, may contain the hydrate or sulphydrate of an alkaline earth-metal; or the hydrate, sulphydrate, carbonate, phosphate,

borate, or silicate of an alkali metal, or some heavy metal dissolved in excess of alkaline hydrate or carbonate (*vide* par. 64).

Solutions which have an acid reaction, known by their reddening blue litmus paper, may contain a free acid, an acid salt, or the normal salt of a heavy metal, in which last case the addition of even a drop of potash will most probably cause a precipitate.

After the above preliminary examination, the solution may be tested according to the directions of Tables I., II., III., and V.; or, in some cases, the evaporated residue may be dissolved in water or acid, and the solution so formed be employed by preference. The original solvent, if suspected to be other than water, may be distilled off, condensed in a receiver, and separately examined.

(64.) Alkaline Solutions of Heavy Metals.

The hydrates of barium, strontium, and calcium, like those of the alkali metals, are soluble in water. The hydrates of all other metals are insoluble, and consequently, precipitable by caustic alkalies. The hydrates of lead, chromium, aluminum, and zinc, are readily soluble in excess of potash or soda; those of silver, copper, cadmium, nickel, cobalt, manganese, zinc, and magnesium readily, and those of chromium and iron (ferrous salts) sparingly soluble in excess of ammonia, especially in presence of neutral ammoniacal salts; while those of bismuth, mercury, and iron (ferric salts), are insoluble in excess of either reagent. On boiling alkaline solutions of chromium, the whole of the chromic hydrate is reprecipitated.

The hydrates of the metals tin, antimony, and arsenic, whose sulphides are soluble in sulphide of ammonium, have no practical interest in analysis. The teroxide of arsenic is slightly soluble in water, and freely soluble in all alkaline liquids. The hydrate of antimony and both hydrates of tin are soluble in excess of potash, while stannic hydrate is soluble also

in excess of ammonia. The potash solution of stannous hydrate is decomposed on boiling into metallic tin, which is deposited as a black powder, and stannate of potassium which remains dissolved.

The precipitates produced by carbonate of ammonium in solutions of silver, copper, nickel, cobalt, zinc, and magnesium, are readily soluble in excess of the reagent, especially when chloride of ammonium is also present, while those of iron (ferrous salts) and chrome are sparingly soluble. The precipitates produced in solutions of cadmium and manganese are insoluble in excess, as are also all those produced in solutions of metals whose hydrates are insoluble in ammonia. The precipitates produced by fixed alkaline carbonates are all insoluble in excess, except that produced in stannic salts, which dissolves in excess of the precipitant, and is again thrown down on ebullition.

§ VIII.—INDIVIDUAL BASES OF GROUP I.

The reactions of the individual bases of this group may be conveniently realized by operating with the following substances:—

Tin . .	The crystallized proto-chloride and precipitated peroxide.
Arsenic .	The white oxide.
Antimony.	The native tersulphide and tartar-emetic.
Bismuth .	The crystallized nitrate aud precipitated oxide.
Mercury .	Corrosive sublimate, the red mercuric oxide, and the crystallized mercurous nitrate.
Lead . .	The oxide, carbonate, nitrate, and acetate.
Silver .	The nitrate aud oxide.
Copper .	The sulphate and oxide.
Cadmium .	The sulphate aud carbouate.

(65.) Tin.

Tin salts are of two kinds, stannous or protosalts, represented by protochloride of tin $SnCl_2$, and stannic or persalts, represented by perchloride of tin $SnCl_4$.

α. When compounds of tin are heated upon char-

coal with a mixture of carbonate of sodium and cyanide of potassium, a globule of white malleable metal is produced with very slight, if any, incrustation. If this globule be hammered out, and dissolved in hydrochloric acid, the tests for stannous salts can be applied to the solution so formed.

Stannous Salts.

α. *Sulphydric acid* produces a brown precipitate of protosulphide of tin SnS, which dissolves in yellow sulphide of ammonium with conversion into persulphide of tin SnS_2, so that on adding an acid to the solution, a yellow and not a brown precipitate is separated. The protosulphide of tin first thrown down is converted by boiling nitric acid into a white insoluble powder consisting of stannic anhydride SnO_2.

β. Solution of *corrosive sublimate*, added carefully to stannous solutions, produces a white precipitate of calomel $HgCl$, which speedily becomes gray, and finally black, from its reduction to the state of metallic mercury.

Stannic Salts.

α. *Sulphydric acid* produces a yellow precipitate of disulphide of tin SnS_2, which is insoluble in the carbonate, but soluble in the hydrate and sulphide of ammonium, and reprecipitable therefrom on the addition of an acid. It is likewise soluble in boiling hydrochloric acid, more readily on the addition of a little nitric acid also, and is converted by concentrated nitric acid into a white insoluble powder of stannic anhydride SnO_2.

(66.) Arsenic.

Arsenious acid is convertible into arsenic acid by boiling it with concentrated nitric acid, to which a

little hydrochloric acid may be added with advantage. But in order to apply the various tests successfully, the acid liquid must be evaporated to dryness, and the residue dissolved in water. Arsenic acid is readily convertible into arsenious acid by the passage of sulphurous acid gas through its solution, or by heating it with sulphite of sodium and dilute hydrochloric acid.

α. *Sulphydric acid* produces, in acidulated solutions of arsenious acid, or of arsenic acid after the addition of sulphurous acid, a yellow precipitate of trisulphide of arsenic As_2S_3, which is soluble in carbonate, hydrate, and sulphide of ammonium, and reprecipitated on the addition of an acid. It is insoluble in boiling hydrochloric acid, but is readily dissolved by hot nitric or nitro-hydrochloric acid.

β. *Nitrate of silver* produces in neutral or slightly ammoniacal solutions of arsenious acid a yellow precipitate of arsenite of silver Ag_3AsO_3, and from similar solutions of arsenic acid a brick-dust red precipitate of arseniate of silver Ag_3AsO_4. Both precipitates are soluble in excess of either ammonia or nitric acid.

γ. *Sulphate of copper* produces, in neutral or very faintly ammoniacal solutions of arsenious acid a grass-green precipitate of arsenite of copper $HCu''AsO_3$, and in similar solutions of arsenic acid a pale blue precipitate of arsenite of copper $Cu''_3(AsO_4)_2$. Both precipitates are soluble in excess of either ammonia or nitric or hydrochloric acid.

δ. When a compound of arsenic is mixed with soda-flux, and heated in a subliming tube, a steel-gray ring of reduced metal condenses in the upper or cool part of the tube.

(67.) Antimony.

α. *Sulphydric acid* produces an orange-colored precipitate of trisulphide of antimony Sb_2S_3, which is

insoluble in carbonate, but soluble in hydrate and sulphide of ammonium, and reprecipitable on the addition of an acid. It is also dissolved by hydrochloric acid with the aid of heat, and is converted almost entirely by strong nitric acid into a white insoluble powder, consisting of tetroxide of antimony Sb_2O_4.

β. *Water*, added to certain antimony solutions (not to all), produces a white precipitate of a basic salt of antimony, soluble in excess of tartaric, hydrochloric, or nitric acid.

γ. Antimony compounds, when fused with carbonate of sodium or charcoal in the reducing flame, yield a bead of brittle metal with an abundant bluish-white incrustation. If the heat be prolonged, the metal volatilizes entirely with the production of white fumes of teroxide of antimony Sb_2O_3.

(68.) Bismuth.

α. *Sulphydric acid* produces a brownish-black precipitate of trisulphide of bismuth Bi_2S_3, which is insoluble in sulphide of ammonium. It dissolves readily in hot nitro-muriatic, nitric, or hydrochloric acid.

β. *Caustic alkalies* give a white precipitate of hydrate bismuth $Bi_2O_3.H_2O$, insoluble in excess of either potash or ammonia.

γ. *Water*, when added to moderately-concentrated and not over-acid solutions of bismuth, causes a dense white precipitate of a basic bismuth salt, which does not disappear on the addition of tartaric acid, but dissolves in excess of nitric or hydrochloric acid.

δ. Bismuth compounds, when mixed with carbonate of sodium and heated upon charcoal in the reducing blowpipe flame, yield a brittle metallic globule and a yellow incrustation.

(69.) Mercury.

There are two classes of mercury salts, namely, the mercurous, represented by calomel HgCl, and the mercuric, represented by corrosive sublimate $HgCl_2$. Certain reactions are common to both, while others are distinctive between them.

α. An excess of *sulphydric acid* produces a black precipitate of mercurous sulphide Hg_2S, or of mercuric sulphide HgS, which is insoluble in sulphide of ammonium, and also in strong hot nitric and hydrochloric acids taken separately, but is readily soluble in a mixture of the two. An insufficiency of sulphydric acid produces in mercuric salts a highly characteristic white precipitate of doubtful composition, which, as the proportion of gas increases, becomes orange, brown, and finally black.

β. *Protochloride of tin* produces at first a white precipitate of calomel HgCl, which becomes in succession gray and almost black on adding more of the reagent and warming gently. If the supernatant liquor be poured off, and the deposit boiled with hydrochloric acid, globules of metallic mercury make their appearance.

γ. Mercury compounds mixed with carbonate of sodium, and heated in a reduction-tube, furnish a sublimate of well-defined mercurial globules.

Mercurous Salts.

α. *Potash* and *ammonia* alike produce a black precipitate, the former of mercurous hydrate $Hg_2O.H_2O$, the latter of some amido-mercurous compound.

β. *Hydrochloric acid* produces a white precipitate of calomel HgCl, which dissolves in boiling nitric acid. It is turned black by ammonia, being converted into amido-mercurous chloride.

MERCURIC SALTS.

α. *Potash* gives a yellow precipitate of mercuric oxide HgO, which is turned white on the addition of ammonia, or in presence of an ammoniacal salt. *Ammonia* produces a white precipitate of some amido-mercuric compound.

β. *Iodide of potassium*, added carefully, produces a bright orange-red precipitate of mercuric iodide HgI_2, which dissolves in excess of the reagent, forming a colorless solution.

(70.) Lead.

α. *Sulphydric acid* produces a black (occasionally red) precipitate of sulphide of lead PbS, which is insoluble in sulphide of ammonium, but dissolves when heated with not too concentrated nitric or hydrochloric acid. Strong nitric acid converts it into a white insoluble deposit of sulphate of lead $PbSO_4$.

β. *Caustic alkalies* give a white precipitate of hydrate of lead $PbO.H_2O$, soluble in excess of potash.

γ. In moderately strong solutions, *hydrochloric acid* gives a white crystalline precipitate of chloride of lead $PbCl_2$, which is soluble in boiling water, unaffected by ammonia, and soluble in great excess of potash.

δ. Dilute *sulphuric acid* or a dissolved sulphate gives a dense white precipitate of sulphate of lead $PbSO_4$, which is insoluble in dilute acids, soluble in strong hydrochloric acid with the aid of heat, and also in a large excess of potash.

ε. Lead compounds, when fused with carbonate of sodium and charcoal in the reducing blowpipe flame, yield a globule of soft metal and a brownish-yellow incrustation.

(71.) Silver.

α. *Sulphydric acid* gives a black precipitate of sulphide of silver Ag_2S, insoluble in sulphide of ammonium, soluble in warm nitric acid, and converted by ebullition with hydrochloric acid into a white deposit of chloride of silver AgCl.

β. *Caustic alkalies* give a brown precipitate of hydrate of silver $Ag_2O.H_2O$, which is insoluble in excess of potash, but soluble in ammonia, forming a colorless solution.

γ. *Hydrochloric acid* gives in solutions of silver salts a white precipitate of chloride of silver AgCl, which is insoluble even in boiling nitric acid, but readily soluble in ammonia. The color of the precipitate changes to a slate-purple by exposure to light.

δ. Silver compounds, when fused with carbonate of sodium upon a charcoal support in the reducing blowpipe flame, yield a button of hard white malleable metal, without any incrustation being formed on the charcoal.

(72.) Copper.

α. *Sulphydric acid* produces a dark-brown precipitate of sulphide of copper CuS, which is insoluble in sulphide of potassium, and but sparingly soluble in sulphide of ammonium. It dissolves readily in nitric but not in hydrochloric acid, save by an application of heat.

β. *Potash* gives a pale blue precipitate of hydrate of copper $CuO.H_2O$, which is insoluble in excess, and converted by ebullition into black oxide of copper CuO. *Ammonia* gives a similar blue precipitate of hydrate of copper, which is soluble in excess of the reagent, forming a deep blue solution, the transparency of which is not affected by the addition of a moderate quantity of potash. The pale blue precipitate pro-

duced by *carbonate of ammonium* is also readily soluble in excess of the reagent, with production of a deep blue liquid.

γ. *Ferrocyanide of potassium* gives a chocolate-colored precipitate of ferrocyanide of copper Cu_2FeCy_6, which is decomposed by caustic potash, and is then freely soluble in ammonia, forming a deep blue liquid.

δ. A piece of clean *iron* or steel dipped into an acidulated copper solution becomes coated with metallic copper, which may be dissolved off by the conjoint action of ammonia and air into a deep blue liquid.

ε. The borax bead heated with a particle of any copper-compound becomes blue or green in the oxidizing, and nearly colorless or reddish-gray in the reducing, flame.

(73.) Cadmium.

α. The precipitate of sulphide of cadmium CdS, produced by *sulphydric acid*, is of a bright yellow color, and insoluble in sulphide of ammonium. It disappears readily on the addition of nitric or hydrochloric acid, and does not form in very acid solutions.

β. *Caustic alkalies* give a white precipitate of hydrate of cadmium $CdO.H_2O$, soluble in excess of ammonia, but not in that of potash. The precipitate produced by carbonate of ammonium does not disappear in excess of the reagent.

γ. Cadmium compounds, fused with carbonate of sodium in the reducing blowpipe flame, give a reddish-brown incrustation of oxide of cadmium CdO, but no bead of metal.

§ IX.—INDIVIDUAL BASES OF GROUP II.

The reactions of the individual bases of this group may be conveniently realized by operating with the following substances:—

NICKEL . .	The oxide and sulphate.
COBALT . .	The oxide.
MANGANESE.	The sulphate, chloride, and carbonate.
IRON . . .	The red and black oxides, the sulphate and sulphide.
ZINC . . .	The oxide and sulphate.
CHROMIUM .	The precipitated oxide and chrome alum.
ALUMINUM .	The hydrate and sulphate.

(74.) NICKEL.

Solutions of nickel are generally of a green color.

α. *Sulphide of ammonium* gives with nickel salts a black precipitate of sulphide of nickel NiS, not soluble in hydrochloric acid until after the addition of a drop or two of nitric acid.

β. *Ammonia* gives a slight greenish precipitate of hydrate of nickel $NiO.H_2O$, soluble in excess of the reagent, forming a violet-blue liquid, from which potash reprecipitates the green hydrate. Moreover, *potash* throws down this hydrate readily from all ordinary nickel solutions.

γ. In the reducing flame, nickel renders the borax bead purplish-gray and turbid, and in the oxidizing flame of a dark sherry color with a tinge of violet. If a fragment of nitre be added, and the bead again heated in the oxidizing flame, a well-marked purple color is produced.

(75.) COBALT.

Cobalt solutions are pink when dilute, blue when concentrated.

α. *Sulphide of ammonium* gives with cobalt salts a black precipitate of sulphide of cobalt CoS, not soluble in hydrochloric acid until after the addition of a few drops of nitric acid.

β. *Potash* gives a blue precipitate of prothydrate of cobalt $CO.H_2O$, insoluble in excess of the precipitant. Excess of *ammonia*, especially in presence of chloride of ammonium, produces a brownish-pink solution,

becoming brown and opaque on exposure to air, from the deposition of the insoluble sesquihydrate.

γ. Cobalt compounds impart to the borax bead, when heated in either flame of the blowpipe, a deep sapphire-blue color.

(76.) Manganese.

Manganese solutions are of a faint pink tinge, or altogether colorless.

α. *Sulphide of ammonium* gives a buff-colored precipitate of sulphide of manganese MnS, soluble even in acetic acid.

β. *Potash* gives a white precipitate of prothydrate of manganese $MnO.H_2O$, speedily becoming brown on exposure, from its conversion into the sesquihydrate $Mn_2O_3.H_2O$. If to the solution of a manganous salt containing chloride of ammonium, an excess of *ammonia* be added at once, a clear colorless solution will be produced, quicky becoming brown and opaque when exposed to the air, from a conversion of the soluble proto- into the insoluble sesqui-compound.

γ. The borax bead with manganese is amethyst-red in the oxidizing, and nearly colorless in the reducing, flame. Its appearance is much interfered with by the presence of a trace of iron.

δ. Compounds of manganese, fused upon platinum foil with *carbonate of sodium* in the oxidizing flame of the blowpipe, either with or without the addition of a little nitre, yield a bluish-green fusible mass of manganate of sodium Na_2MnO_4. For this experiment but a very small quantity of the manganese compound should be employed.

(77.) Iron.

There are two classes of iron salts, namely, ferrous or protosalts, represented by green vitriol $FeSO_4$, and ferric or persalts, represented by sesquichloride

of iron $FeCl_3$ or Fe_2Cl_6. The protosalts are rarely ever free from some admixture with persalts.

α. *Sulphide of ammonium* gives a black precipitate of protosulphide of iron FeS, readily soluble in hydrochloric acid. The precipitate, when thrown down from ferric salts, is accompanied by free sulphur.

β. Iron compounds dissolve in the borax bead, forming a glass which is of a bottle-green color in the reducing, and of a yellowish-brown color in the oxidizing, flame. Ferrous compounds give the green, and ferric compounds the yellow, color most readily.

FERROUS SALTS.

Ferrous solutions are generally colorless, or of a pale green tint.

α. *Caustic alkalies* give a dingy green precipitate of ferrous hydrate $FeO.H_2O$, which becomes red on exposure to air. The pure, nearly white prothydrate is sparingly soluble in excess of ammonia and chloride of ammonium.

β. *Ferrocyanide of potassium* gives a pale blue precipitate of double ferrocyanide of iron and potassium $K_2Fe_2Cy_6$, which becomes dark blue on exposure to air.

γ. *Ferridcyanide of potassium* gives a dark-blue precipitate of ferridcyanide of iron Fe_5Cy_{12}, or $Fe''_3 Fe_2'''Cy_{12}$, insoluble in dilute acids and decomposable by caustic alkalies.

FERRIC SALTS.

Ferric solutions are generally of a yellow, brown, or red color.

α. *Caustic* and *carbonated alkalies* alike give a brick-dust red precipitate of ferric hydrate $Fe_2O_3.H_2O$, accompanied in the case of the carbonates by an evolu-

tion of carbonic acid. The precipitate is quite insoluble in the hydrates of potassium and ammonium, and also in their respective carbonates at a boiling heat.

β. *Ferrocyanide of potassium* gives a deep blue-colored precipitate of sesquiferrocyanide of iron Fe_7Cy_{18}, or $Fe''_3Fe'''_4Cy_{18}$, insoluble in dilute acids, and decomposable by caustic alkalies. The ferridcyanide does not produce any precipitate, but gives to the ferric solution a color which is brown or red according to circumstances.

γ. *Sulphocyanate of potassium* imparts to ferric solutions a deep red color, from the formation of ferric sulphocyanate $FeCy_3S_3$, or $Fe(CyS)_3$.

(78.) Zinc.

Zinc solutions are usually colorless.

α. *Sulphide of ammonium* gives a white precipitate of sulphide of zinc ZnS, which is insoluble in acetic, but readily soluble in hydrochloric, acid. Unlike most zinc precipitates, it is insoluble in any alkaline solution.

β. *Caustic alkalies* give with solutions of zinc a white precipitate of hydrate of zinc $ZnO.H_2O$, soluble in a large excess of the precipitant. *Alkaline carbonates* also give a white precipitate of a highly basic carbonate of zinc, insoluble in excess of the fixed alkaline carbonates, but soluble in presence of ammoniacal salts.

γ. Zinc salts, heated on platinum foil, leave a fixed infusible residue, which is yellow when hot, white when cold. After being moistened with solution ot nitrate of cobalt, and reignited in the blowpipe flame, it assumes a fine green color.

δ. Zinc salts, mixed with carbonate of sodium or cyanide flux, and heated in the reducing blowpipe flame, deposit upon the charcoal an incrustation which

is yellow when hot, white when cold, and green after ignition with nitrate of cobalt.

(79.) Chromium.

Solutions of chromic salts are mostly of a green or violet color.

α. *Caustic alkalies*, their *sulphides* or *sulphydrates*, and *carbonates* throw down from chrome solutions a greenish precipitate of hydrate of chrome $Cr_2O_3.H_2O$, which is slightly soluble in excess of ammonia, more so in excess of potash, and in each instance reprecipitable on boiling. Its production by sulphides and carbonates respectively is accompanied by an evolution of sulphydric or carbonic acid.

β. Chrome imparts to the borax bead a fine green color, permanent in both flames of the blowpipe.

γ. When a chrome compound is fused on platinum foil with a little carbonate of sodium and nitre, a yellow mass of chromate of sodium Na_2CrO_4, is produced, which dissolves in water to form a solution, giving with acetate of lead a yellow precipitate of chromate of lead $PbCrO_4$.

(80.) Aluminum.

α. *Caustic alkalies*, their *carbonates* and *sulphides* or *sulphydrates*, give with aluminous solutions a white gelatinous precipitate of hydrate of aluminum $Al_2O_3.H_2O$, which is soluble in excess of potash, but reprecipitated on the addition of chloride of ammonium. The action of the carbonates and sulphides respectively is accompanied by an evolution of carbonic or sulphydric acid.

β. Salts of aluminum, when heated on charcoal or platinum foil, leave a white, infusible, highly incandescent residue, which, when moistened with nitrate of cobalt solution and reignited in the blowpipe flame, assumes a bright blue color.

§ X.—INDIVIDUAL BASES OF GROUP III.

The reaction of the individual bases of this group may be conveniently realized by operating with the following substances :—

Barium . .	The carbonate, nitrate, and chloride.
Strontium .	The carbonate and nitrate.
Calcium . .	The hydrate, carbonate phosphate, oxalate, and sulphate.
Magnesium .	The oxide, carbonate, and sulphate.
Potassium .	The nitrate and sulphate.
Sodium . .	The carbonate, sulphate, chloride, and phosphate.
Ammonium .	The sulphate, chloride, carbonate, phosphate, and oxalate.

(81.) Barium, Strontium, Calcium.

These three metals possess many properties in common.

α. Their hydrates $MO.H_2O$ or $M(HO)_2$. are all soluble in water, so that the addition of caustic alkali, if perfectly free from carbonate, does not disturb their solutions. Their sulphides and sulphydrates are also soluble.

β. The following salts of these metals are insoluble in water, namely, the oxalates, phosphates, carbonates (even in the presence of ammoniacal salts), and sulphates, sulphate of barium being the most insoluble, sulphate of calcium the least so. Hence neutral barium, strontium, and calcium salts are precipitated by soluble oxalates, phosphates, carbonates, and sulphates.

γ. When a barium, strontium, or calcium salt is ignited on platinum foil, a white fixed residue remains, which, except in the case of the chlorides, is usually infusible. When moistened with solution of nitrate of cobalt and reignited, the infusible mass acquires an ill-defined gray color.

(82.) Barium.

α. *Sulphuric acid* and solutions of all *sulphates*, even when very dilute, give with barium salts a white precipitate of sulphate of barium $BaSO_4$, insoluble in acids and alkalies.

β. *Hydrofluosilicic acid* produces in acid and neutral solutions a somewhat transparent precipitate of fluosilicate of barium $BaSiF_6$, the deposition of which is much facilitated by the addition of a little alcohol.

γ. Barium salts, when intensely heated before the blowpipe upon a fine platinum wire, impart a marked apple-green color to the flame.

(83.) Strontium.

α. *Sulphuric acid* and solutions of most *sulphates*, give a precipitate of sulphate of strontium $SrSO_4$, insoluble in acids and alkalies, very sparingly soluble in water. Strontium salts are not precipitated by solution of sulphate of strontium, and very slowly by solutions of the sulphates of calcium and potassium.

β. Strontium salts when intensely heated before the blowpipe upon a fine platinum wire, impart a deep crimson color to the flame.

(84.) Calcium.

α. *Sulphuric acid* and strong solutions of *sulphates* give with moderately strong calcium solutions a white precipitate of sulphate of calcium $CaSO_4$, slightly soluble in water, insoluble in proof-spirit. But dilute calcium solutions are not precipitable by any sulphate; while even strong solutions are not precipitable by the sulphates of strontium, calcium, and scarcely by that of potassium.

β. *Oxalate of ammonium* produces in neutral calcium solutions a white precipitate of oxalate of calcium CaC_2O_4, soluble in nitric and hydrochloric acids, in-

soluble in acetic and oxalic acids, and insoluble in ammonia.

γ. Calcium salts impart a fine orange-red color to the blowpipe flame.

(85.) Magnesium.

α. Sulphydrate and sulphate of magnesium are soluble in water. Hence magnesian salts are not precipitated by soluble sulphydrates and sulphates.

β. Hydrate, carbonate, oxalate, phosphate, and arseniate of magnesium, are insoluble in water. Hence magnesian salts are precipitated by soluble hydrates, carbonates, oxalates, phosphates, and arseniates. But all magnesian precipitates, excepting the phosphate and arseniate, are soluble in ammoniacal solutions. When *phosphate of sodium* or *ammonium* is added to a solution of magnesium containing chloride of ammonium and rendered alkaline by ammonia, a white crystalline precipitate of triple phosphate $Mg(NH_4)PO_4$, is produced, which is soluble in dilute acids, insoluble in ammonia and ammoniacal salts.

γ. Magnesian compounds, heated on charcoal or platinum foil, leave a white fixed infusible residue, which when moistened with nitrate of cobalt solution and reignited in the blowpipe flame assumes a faint pink color.

(86.) Potassium.

α. All simple potassium salts, except the acid-tartrate, are moderately soluble in water. *Tartaric acid* added in excess to the neutral or alkaline solution of a potassium salt throws down a white crystalline precipitate of cream of tartar $KH_4C_4O_6$, which frequently does not appear immediately. Its deposition is facilitated by stirring the mixed liquids, and by the addition of a little alcohol to them. It is soluble in

mineral acids, in hot water, and in a large excess of cold water.

β. *Perchloride of platinum* when added to neutral or acid solutions of potassium throws down a yellow crystalline precipitate of potassio-chloride of platinum K_2PtCl_6, or $2KCl.PtCl_4$. The solution should generally be acidulated with a few drops of hydrochloric acid before being tested. The precipitate does not always appear immediately: its production is facilitated by stirring, and by the addition of a little alcohol.

γ. Potassium salts when heated on charcoal or platinum foil leave a fixed and generally fusible residue. When heated before the blowpipe they impart to the flame a marked violet color, which, however, is not recognizable in the presence of even a small quantity of sodium.

(87.) Ammonium.

α. All simple ammoniacal salts, except the acid tartrate, are freely soluble in water. *Tartaric acid* reacts upon ammoniacal as upon potassium salts. The resulting precipitate of acid tartrate of ammonium $(NH_4)H_5C_4O_6$, is, however, more soluble in water than the corresponding potassium compound, and consequently does not form, save when the ammoniacal solution is moderately concentrated.

β. *Perchloride of platinum* reacts upon ammoniacal salts to form the ammonio-chloride of platinum $(NH_4)_2PtCl_6$, or $2NH_4Cl.PtCl_4$, which closely resembles the corresponding potassium compound in its appearance, solubility, and mode of deposition.

γ. When any ammoniacal salt is boiled with *potash* or *lime*, ammoniacal vapor is given off, which is recognizable by its smell, by its action on test paper, and by its forming opaque fumes when brought into contact with the vapor of hydrochloric acid.

δ. All ammoniacal salts volatilize partly, most of

them entirely, when heated upon platinum foil or charcoal.

(88.) Sodium.

a. Sodium solutions are non-precipitable, all simple sodium salts being soluble in water.

β. Sodium salts when heated on platinum foil or charcoal leave a fixed residue, almost always fusible, and impart an intense yellow color to flame.

§ XI.—REACTIONS OF INDIVIDUAL ACIDS.

(89.) Chromates.

Chromates are usually of a yellow or red color, and, except those of the alkali metals, are more or less insoluble in water.

a. Chromates acidified with hydrochloric acid, and treated with *sulphuretted hydrogen*, yield a deposit of sulphur, and a green solution of chromic chloride, $CrCl_3$ or Cr_2Cl_6. The same compound is produced on boiling the solution of a chromate with hydrochloric acid and a little alcohol. To it the ordinary tests for chrome salts can be applied.

β. *Nitrate of silver* gives a dark red precipitate of chromate of silver Ag_2CrO_4, soluble in nitric acid. *Nitrate of barium* and *acetate of lead* throw down yellow precipitates of the chromates of the respective metals.

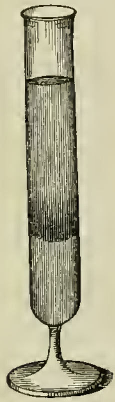
(90.) Nitrates.

The nitrates are soluble or non-precipitable salts, which deflagrate when ignited upon charcoal or with organic matter.

a. When a nitrate, or the concentrated solution of a nitrate, is gently heated with *sulphuric acid* and a

few *copper turnings*, brown fumes of peroxide of nitrogen N_2O_4, are evolved, which redden, but do not bleach, litmus paper, and produce a purple coloration on starch paper moistened with iodide of potassium.

Fig. 36.



β. A solution of *protosulphate of iron* carefully poured upon *sulphuric acid*, to which a minute portion of a solid or dissolved nitrate has been added, produces a deep brown halo at the junction of the two liquids, as seen in Fig. 36.

γ. When a minute quantity of *gold-leaf* is boiled in *hydrochloric acid*, no action is produced; but, on the addition of a little nitric acid or a nitrate, the gold quickly disappears, and may be detected in solution by protochloride of tin, which gives rise to a purplish precipitate.

(91.) Chlorates.

The chlorates, like the nitrates, are soluble or non-precipitable salts, which deflagrate when ignited upon charcoal or with organic matter.

α. Strong *sulphuric acid* added to a solid chlorate produces a brown coloration with crackling detonation, especially when gently warmed. The experiment should be made carefully, and with but a small quantity of the salt, for fear of an explosion and scattering of the acid.

β. The addition of some solid or dissolved chlorate to *hydrochloric acid* enables it to bleach litmus and dissolve gold-leaf. Strong hydrochloric acid reacts with a moderate quantity of a solid chlorate to produce a greenish-yellow gas known as euchlorine.

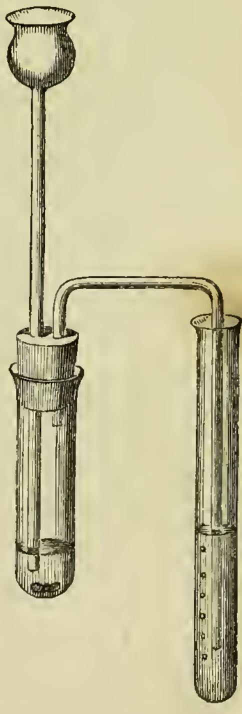
γ. Chlorates of alkali-metal, when heated alone, and other chlorates, when heated with carbonate of sodium

in a reduction tube, evolve oxygen, known by its inflaming a piece of incandescent wood; and leave a residue of alkaline chloride, recognizable by adding nitrate of silver to its solution previously acidified with nitric acid, when a white precipitate of chloride of silver is thrown down.

(92.) CARBONATES.

On adding *hydrochloric* or slightly diluted *sulphuric acid* to a solid or dissolved carbonate, effervescence of carbonic anhydride CO_2, is produced, either immediately or on gently warming. The gas is free from any marked smell, and does not affect lead paper, but turns *lime water* milky, from the precipitation of carbonate of calcium $CaCO_3$. It may be tested by means of the apparatus shown in Fig. 37; or, being one and a half times as heavy as air, it may be generated in one test tube, and then carefully poured into another containing some lime water, with which it is to be agitated. The lime water may be replaced by baryta-water or a solution of basic acetate of lead.

Fig. 37.



β. Soluble carbonates give precipitates with salts of silver, barium, calcium, &c. &c., which disappear with effervescence on the addition of any acid.

(93.) Sulphides and Sulphydrates.

α. Most sulphides when acted upon by hydrochloric or moderately dilute sulphuric acid, especially on the application of heat, evolve sulphuretted hydrogen, which is known by its offensive smell, and by the brown or lustrous black stain it produces on lead paper. All sulphides, when fused with earbonate of sodium in a porcelain capsule, leave a residue which disengages sulphuretted hydrogen upon the addition of an acid. The residue, moistened with water, gives a black stain to silver coin, and a purple coloration with nitroprusside of sodium (*vide* β and γ).

β. Soluble sulphides, including sulphide of hydrogen, give with *nitrate of silver* a black precipitate of sulphide of silver Ag_2S, which does not disappear on the addition of cold nitric acid. They also produce a black stain on metallic silver, or *acetate of lead* paper. The precipitate of sulphide of lead PbS, thrown down from any dissolved lead salt, is not affected by dilute mineral acids, save on the application of heat.

γ. *Nitroprusside of sodium* produces a magnificent purple coloration with soluble sulphides, even when extremely dilute. The effect, however, is not obtained with sulphide of hydrogen until after the addition of a drop or so of alkali.

δ. Many sulphides, when heated in a glass tube open at both ends, evolve sulphurous anhydride SO_2, which is known by its smell of burning sulphur, and by its producing a purple stain on starch paper moistened with iodic acid.

(94.) Sulphites.

α. *Hydrochloric* or *sulphuric acid* causes an effervescence of sulphurous acid or anhydride SO_2, known by its smell of burning sulphur, and by the purple coloration it gives to starch paper moistened with iodic acid. On the addition of a fragment of zinc, the

sulphurous is replaced by sulphydric acid, known by its effect on lead paper. **Hyposulphites** behave in a similar manner, except that the effervescence of sulphurous acid is accompanied by a deposition of yellow sulphur.

β. *Perchloride of iron* produces in neutral solutions a red coloration, which disappears on the addition of a strong acid, and is destroyed by boiling, with formation of a brown deposit of ferric oxide.

(95.) Sulphates.

α. *Nitrate* or *chloride of barium* throws down an opaque white precipitate of sulphate of barium $BaSO_4$, which does not disappear on the addition of hydrochloric or nitric acid even at a boiling heat. But in presence of a large excess of nitric acid a portion of sulphate of barium remains in solution. The seleniate and silicofluoride of barium resemble the sulphate in being precipitable from acid solutions; but, when boiled with strong hydrochloric acid, the seleniate dissolves with evolution of chlorine, while the silicofluoride, which is very transparent, dissolves, with the exception of a little silica.

(96.) Chlorides.

α. *Nitrate of silver* produces a white clotty precipitate of chloride of silver AgCl, which becomes slate-colored on exposure to light. It is insoluble even in boiling concentrated nitric acid, but is readily soluble in ammonia. When heated in a porcelain capsule, it does not undergo decomposition, but simply fuses.

β. Chlorides, when heated with strong *sulphuric acid*, save those of mercury, silver, and tin, evolve hydrochloric acid gas, known by its pungent smell and acid reaction. When heated with *peroxide of manganese* and sulphuric acid, chlorine gas is given off, recognizable by its irritant odor, green color, power of bleaching litmus, &c., and by the purple

stain it produces on a piece of starch paper moistened with iodide of potassium.

(97.) Bromides.

α. The precipitate of bromide of silver $AgBr$, produced by *nitrate of silver* in solutions of bromides, closely resembles the chloride, except that it has a faint tinge of yellow and is less readily soluble in ammonia.

β. Bromides when heated with strong *sulphuric acid*, with or without the addition of *peroxide of manganese*, evolve bromine, which is recognized by the red color and irritant smell of its vapor, by its bleaching litmus, and turning starch paper yellow.

(98.) Iodides.

α. The precipitate of iodide of silver AgI, produced by *nitrate of silver* in solutions of iodides, is of a pale yellow color, insoluble in, but turned white by, ammonia, and in other respects similar to the chloride.

β. A sufficiency of *chloride of mercury* produces a scarlet precipitate of iodide of mercury HgI_2; while *acetate of lead* throws down a yellow precipitate of iodide of lead PbI_2, somewhat soluble in boiling water, and deposited therefrom on cooling, in golden scales.

γ. Iodides when acted upon by strong *sulphuric acid* with or without *peroxide of manganese*, evolve iodine, known by its violet vapor, staining starch paper purple.

δ. A drop or two of *chlorine* water, or of nitric or preferably nitro-hydrochloric acid, added to a dissolved iodide, causes a liberation of its iodine, which, if in any quantity, imparts a yellow-brown color to the liquid. But in presence of dilute starch paste, a deep purple color is developed; and chloroform or disulphide of carbon shaken with the liquid becomes of a bright pink or crimson color.

(99.) CYANIDES.

α. *Nitrate of silver* throws down a white clotty precipitate of cyanide of silver AgCl, not altered in color by exposure to light. It is readily soluble in ammonia, insoluble in cold, but soluble in boiling concentrated nitric acid.

The white precipitates produced by nitrate of silver in **ferrocyanide** and **sulphocyanate** solutions, and the brown precipitate produced in **ferridcyanide** solutions are insoluble in nitric acid.

β. When a mixture of ordinary *sulphate of iron* and *potash* is added to a simple cyanide, no obvious effect is produced, but on acidification with hydrochloric acid the unaltered hydrates of iron are dissolved, and Prussian blue or sesquiferrocyanide of iron, Fe_7Cy_{18} or $Fe_3''Cy_6$, $Fe_4'''Cy_{12}$, is left as a deep blue precipitate.

γ. Cyanides, including cyanide of silver, when acted upon by yellow *sulphide of ammonium*, are converted into sulphocyanates $MCyS_2$. After evaporating to dryness, to expel the excess of sulphide of ammonium, *perchloride of iron* gives a deep red coloration due to the production of ferric sulphocyanate $Fe'''(CyS)_3$.

(100.) PHOSPHATES.

α. *Sulphate of Magnesium* added to a phosphate solution rendered alkaline by ammonia, and containing chloride of ammonium, produces a white crystalline precipitate of phosphate of magnesium and ammonium $Mg(NH_4)PO_4$, readily soluble in acids. The formation of the precipitate is facilitated by rubbing the inside of the tube with a stirring rod. *Chloride of barium* or *calcium* produces in neutral or ammoniacal phosphate solutions a white precipitate of phosphate of calcium or barium, soluble even in acetic acid.

β. *Nitrate of silver* added to a neutral or nearly neutral phosphate solution, produces a yellow (under certain circumstances white) precipitate of phosphate of silver Ag_3PO_4, soluble in ammonia and dilute nitric acid.

γ. *Perchloride of iron* produces in phosphate solutions which are neutral, or acid only with acetic acid, a pale brown precipitate of phosphate of iron $Ffe'''PO_4$. An excess of acetate of ammonium may be added to a solution of phosphate of magnesium or calcium in the smallest sufficient quantity of hydrochloric acid, whereby the free hydrochloric is replaced by free acetic acid. Then, on adding a drop of perchloride of iron, a deep red color, speedily changing into an opaque white cloud, is produced. On adding more perchloride of iron gradually, until the liquid remains permanently red, and afterwards boiling and filtering, a colorless filtrate is obtained, free alike from phosphoric acid and iron, but containing chloride of calcium or magnesium.

δ. Excess of *molybdate of ammonium* added to a phosphate solution containing free nitric acid, produces, either immediately or on gentle warming, a bright yellow precipitate of a phospho-molybdate of ammonium of uncertain composition.

Except that the arseniate of silver is brick red instead of yellow or white, all the above described reactions apply equally to arsenic and phosphoric acids. Arsenic acid may, however, be got rid of by treatment of its solution with sulphurous acid and sulphydric acid in succession, or by prolonged treatment with sulphydric acid alone (*vide* par. 66).

(101.) Oxalates.

Unlike most organic acids, save those which volatilize without decomposition, neither oxalic acid nor its salts become charred by the action of heat or strong

sulphuric acid. They effervesce with dilute sulphuric acid and peroxide of manganese.

α. Oxalates soluble in water, or oxalates soluble in acid after the addition of acetate of ammonium, give with *chloride* or even *sulphate of calcium* a white precipitate of oxalate of calcium CaC_2O_4, insoluble in ammonia and in acetic acid, but soluble in dilute mineral acids.

β. *Nitrate of silver* and *chloride of barium* give with neutral oxalates white precipitates of oxalates of silver $Ag_2C_2O_4$, and oxalate of barium BaC_2O_4, respectively, soluble in dilute nitric, but insoluble or very sparingly soluble in acetic acid.

(102.) TARTRATES.

Tartaric acid and tartrates, when ignited, evolve a peculiar odor, and leave an abundant charcoal. They become blackened when heated with strong sulphuric acid; whereas citric acid and the citrates acquire only a yellow color.

α. *Chloride of calcium* produces in neutral tartrates a white precipitate of tartrate of calcium $Ca''H_4C_4O_6$, soluble even in acetic acid. On heating the washed precipitate with aqueous potash, filtering the mixture and boiling the filtrate, a white turbidity is produced which disappears on cooling. Chloride of calcium does not precipitate neutral citrates in the cold; but, upon boiling, a temporary white turbidity is produced.

β. *Nitrate of silver* throws down from neutral tartrates a white precipitate of tartrate of silver $Ag_2H_4C_4O_6$, soluble in dilute nitric acid and in ammonia, and decomposed on boiling, with blackening and reduction. *Chloride of barium* does not precipitate tartrates in the presence of ammoniacal salts or free acid.

γ. Neutral tartrates of potassium, and of sodium and ammonium in presence of *chloride of potassium*,

yield, on acidification with *acetic acid*, a white crystalline precipitate of cream of tartar, or acid tartrate of potassium $KH_5C_4O_6$, which deposits most readily on stirring, and is soluble in boiling water and mineral acids.

(103.) Acetates.

α. *Perchloride of iron* added to a neutral acetate produces a deep red color, from the formation of peracetate of iron $Fe'''(H_3C_2O_2)_3$. The color is destroyed on the addition of a mineral acid, or on boiling; in the latter case with formation of an ochry deposit.

β. *Nitrate of silver* produces, in concentrated solutions only, a white precipitate of acetate of silver $AgH_3C_2O_2$, soluble in hot water, in dilute nitric acid, and in ammonia.

γ. On warming a solid acetate, or its concentrated solution, with *sulphuric acid*, acetic acid is liberated, recognizable by its well-known smell; but in presenee of *alcohol* the fragrant vapor of acetic ether $(C_2H_5)H_3C_2O_2$, is evolved instead.

(104.) Benzoates.

Benzoates evolve the characteristic smell of benzene upon ignition, and yield a sublimate of benzoic acid when warmed with strong sulphuric acid; but in neither case do they undergo much charring.

α. *Perchloride of iron* gives with neutral benzoates a brownish yellow precipitate of perbenzoate of iron $Fe'''(H_5C_7O_2)_3$, which dissolves completely in warm dilute hydrochloric acid forming a solution from which benzoic acid crystallizes out on calling.

β. *Nitrate of silver* gives a white clotty precipitate of benzoate of silver $AgH_5C_7O_2$, soluble in hot water, in dilute nitric acid, and in ammonia.

(105.) BORATES.

Borate solutions have usually an alkaline reaction to test-paper. Several borates are sparingly soluble, but none of them insoluble in water; whence dilute solutions of borates are non-precipitable.

α. *Alcohol* added to a mixture of sulphuric acid and a borate, burns with a marked green flame, the color of which is best brought out on stirring the burning mixture.

β. The solution of a borate, acidified with hydrochloric acid, has the property of turning *turmeric paper* of the brown color usually caused by alkalies. Even with dilute solutions the coloration becomes well marked on drying the paper. The acidification if not too dilute borate solutions is attended with the precipitation of boric or boracic acid H_3BO_3.

(106.) FLUORIDES.

α. Fluorides, when gently heated with strong *sulphuric acid*, evolve hydrofluoric acid vapor HF, which becomes opaque in moist air, and has a very pungent, irritating smell. The experiment is best made in a platinum crucible, but should a test-tube or watch-glass be employed, its interior will afterwards be found corroded. When a piece of flat glass, covered with a layer of beeswax, through which some markings have been scratched, is exposed for a little while to the action of the vapor, the markings become permanently etched upon the glass, and even if very slight may be rendered evident by breathing upon its well-polished surface.

β. Fluorides, mixed with *silica* or any silicate, and warmed with *sulphuric acid*, evolve gaseous fluoride of silicon SiF_4, as a pungent, irritating gas, rendered opaque and acid by moist air, in consequence of the following decomposition:—

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3 \text{ or } H_2O.SiO_2.$$

Hence the wetted surface of a strip of glass, dipped into the gas, or the moist interior of a tube through which it is transmitted, as shown in Fig. 38, soon acquires an opaque coating of silica.

γ. The soluble fluorides of potassium and sodium give with *chloride of calcium* or *chloride of barium* a gelatinous white precipitate, soluble in hydrochloric acid, slightly soluble in ammoniacal salts, and scarcely at all soluble in acetic acid; though, indeed, the precipitated fluoride of calcium CaF_2, or of barium BaF_2, is often accompanied by some silicofluoride insoluble in hydrochloric acid. Fluor-spar, or native fluoride of calcium, is not readily soluble in hydrochloric acid, but an available solution may be obtained by digesting the finely-powdered spar for some time in the strong acid, and then boiling the mixture after dilution with water.

Fig. 38.

(107.) Silicates.

Silicates of potassium and sodium, when not containing an excess of silica, are soluble in water, but all other silicates are insoluble.

α. On acidifying the solution of a silicate of alkali-metal with *hydrochloric acid* complete decomposition takes place, most usually with precipitation of some silicic acid in the gelatinous form, while another portion remains dissolved in the acid liquid. Under certain circumstances, however, as when the silicate soluble is rather dilute, or when it is added at once to an excess of hydrochloric acid, there may not be any precipitation whatever. But in any case, upon evaporating down the clear acidified solution, the whole of the dissolved silicic acid separates out in the form of silica, which, after drying, is insoluble both in acid and alkaline solutions. The precipitate of gelatinous silicic acid is readily soluble in solutions of caustic alkali, and

even of carbonated alkali when gently warmed therewith; but upon drying at a moderate heat, it becomes hard, gritty, and insoluble.

β. Owing to the incompetency of silicic acid to form a salt with ammonia, *chloride* or *carbonate of ammonium* added to a dissolved silicate of alkali-metal precipitates gelatinous silica, which separates more completely on evaporation, at the same time becoming anhydrous.

γ. *Carbonate of sodium* fused before the blowpipe on a loop of platinum wire furnishes a bead which is transparent while hot, opaque when cold; but a little silica added to the strongly heated bead dissolves therein with effervescence, and, if in sufficient quantity, renders it permanently transparent.

CHAPTER III.

TOXICOLOGICAL CHEMISTRY.

(108.) For the performance of this part of the course, the student should be provided in succession with the principal poisons in the various forms in which they ordinarily occur in medico-legal practice. He must examine each poison in the several conditions in which it is presented to him, and verify all its described reactions. The different poisons may be met with in the ordinary state in which they are sold; dissolved in or diluted with water; in various organic liquids, either the vehicles in which they were administered, or the contents of the stomach for instance; mixed with solid food; in the tissues of different organs, more particularly the liver and kidney; and as stains upon clothing. They may be roughly classified into acid poisons, including the sulphuric, nitric, hydrochloric, and oxalic acids; metallic poisons, including compounds of mercury, lead, copper, arsenic, and antimony; and organic poisons, including prussic acid, strychnia, and opium.

§ I.—SULPHURIC ACID.

(109.) Concentrated.

α. **Appearance.** Concentrated sulphuric acid, or oil of vitriol, occurs as a heavy, somewhat oily liquid, usually having a more or less marked brownish tint.

β. **Volatility.** A few drops of the acid, when cautiously heated upon a watch-glass, or on platinum foil, disappear entirely with the formation of opaque white acrid fumes.

γ. **Heat on admixture with water.** Upon agitating a drachm or so of the strong acid with about an equal bulk of water, the temperature of the mixture rises very considerably, and the outside of the tube or other containing vessel becomes insupportably hot to the hand.

δ. **Charring organic matter.** A piece of paper, wood, or sugar, dipped into the strong acid, speedily becomes blackened or carbonized.

ε. **Evolution of sulphurous acid.** Upon gently heating sulphuric acid in a test tube with some chips of wood, copper turnings, or mercury, a vapor having the peculiar suffocating smell of burning sulphur is evolved; while a piece of starch-paper, moistened with iodic acid solution and held over the mouth of the tube, acquires a purple color, which, however, the prolonged action of the vapor ultimately causes to disappear.

(110.) Diluted.

α. **Acid reaction, &c.** Dilute sulphuric acid is entirely volatilizable by heat, has a marked acid reaction to test paper, and dissolves a fragment of carbonate of ammonium or sodium with rapid effervescence.

β. **Charring after concentration.** Marks upon paper made with the dilute acid appear simply wet, but become gradually black from carbonization, on carefully drying the paper over a stove or gas flame.

γ. **Precipitation of sulphate of barium.** Solution of nitrate or chloride of barium throws down from dilute sulphuric acid a white precipitate of sulphate of barium, not affected by the addition of nitric or hydrochloric acid.

δ. **Recognition of sulphur in precipitate.** The precipitate having been collected on a filter, is washed, dried, and intimately mixed with about an

equal quantity of black flux. The mixture is then heated to redness in a reduction tube or before the blowpipe, whereby a fused residue is obtained, from which hydrochloric acid causes an evolution of sulphuretted hydrogen gas, recognizable by means of lead paper, to which it imparts a glistening black or brown discoloration.

(111.) In Organic Liquids.

a. Sulphuric acid contained in an organic liquid, such as coffee, beer, or the contents of the stomach, readily manifests all the above described properties of the dilute acid, except that of volatility. Should the liquid be viscid or turbid, it must be diluted freely with water or proof spirit, and strained through fine muslin, or, if practicable, filtered through paper. The filtrate is precipitable by nitrate or chloride of barium (*vide* 110); and upon being evaporated down, becomes more strongly acid, chars, and evolves sulphurous acid gas (*vide* 109). Although, from the administration of antidotes in cases of sulphuric acid poisoning, the contents of the stomach or vomited matters may not exhibit any, or only a very slight acid reaction, they may, nevertheless, yield an abundant precipitate of sulphate of barium.

(112.) Stains on Clothing.

a. The concentrated acid produces, upon black cloth, for instance, a brown stain with or without a red border; and the diluted acid a red stain, gradually becoming brown. The stains remain moist for a long time, and in all cases the fibre becomes destroyed with greater or less rapidity. By treating the stained pieces with water, a solution of sulphuric acid is obtained, which manifests acidity to test paper, and yields a white precipitate with nitrate of barium. A portion of the stained stuff heated in a reduction tube evolves sulphurous acid, recognizable by its

smell, and by its reaction upon starch paper moistened with iodic acid solution.

§ II.—NITRIC ACID.

(113.) Concentrated.

α. **Appearance.** Nitric acid when pure is colorless; but when containing peroxide of nitrogen is straw-yellow or orange, and somtimes even green or blue.

β. **Volatility.** The concentrated acid when exposed to the air at ordinary temperatures gives off colorless or orange fumes, having a characteristic smell, and a strongly marked acid reaction. A few drops of the acid heated upon a watch-glass disappear without leaving any residue.

γ. **Action on organic matter.** A strip of flannel or other nitrogenized organic tissue dipped into strong nitric acid becomes stained distinctly yellow; the color being rendered darker and browner by the subsequent action of caustic alkali. Black and colored cloths likewise become stained of a yellow color, and rapidly corroded by a strong acid.

δ. **Action on metals.** When nitric acid is gently warmed in a test-tube with a drop or two of mercury or a few copper-turnings, violent chemical action takes place, as evidenced by the solution of the metal, and the copious evolution of orange-brown vapors which redden but do not bleach litmus paper, and produce a purple coloration on starch paper moistened with iodide of potassium.

ε. **Reaction with sulphate of iron.** Nitric acid added to a cold moderately concentrated solution of sulphate of iron, produces a dark greenish-brown discoloration, which disappears on the application of heat with evolution of orange fumes.

ζ. **Solution of gold.** Gold leaf is unacted upon by boiling nitric acid, but upon the addition thereto of a little hydrochloric acid it undergoes rapid solution.

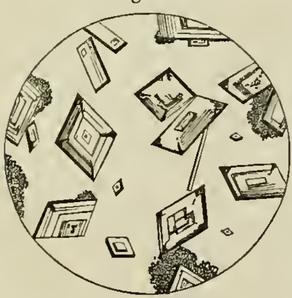
(114.) Diluted.

α. **Acid reaction, &c.** Dilute nitric acid is completely volatilized by heat; has a marked acid reaction; when evaporated from paper moistened with it, does not leave a black, but only a slightly yellow stain; produces upon black cloth a stain, red at first, but ultimately yellow; and, if pure, gives no precipitate with solutions of chloride of barium and nitrate of silver respectively. When neutralized by the hydrate or carbonate of sodium, potassium, or barium, it is converted into a nitrate which may be obtained solid and crystalline by careful evaporation.

(115.) Nitrates.

α. **Crystalline form.** A drop or so of the aqueous solution of a nitrate heated slowly upon a glass plate until a solid margin appears round the edge of the liquid, yields upon cooling a well crystallized residue, which may be examined by a pocket lens or the low power of a microscope. The potassium salt crystallizes in long fluted six-sided prisms, the sodium salt (Fig. 39), in rhombic plates, and the barium salt in octahedrons.

Fig. 39.



β. **Deflagration with charcoal.** A solid nitrate heated upon charcoal, or heated with charcoal powder on platinum foil, undergoes deflagration; while a

piece of filtering paper moistened with the solution of a nitrate and dried, burns in the characteristic manner of touch paper.

γ. **Evolution of peroxide of nitrogen.** When a mixture of a little powdered nitrate with a few copper filings is acted upon by sulphuric acid and gently warmed, orange-brown fumes are given off, which redden but do not bleach litmus paper, and produce a purple coloration on starch paper moistened with iodide of potassium. This experiment may be performed satisfactorily with less than one-tenth of a grain of nitre.

δ. **Reaction with sulphate of iron.** When a solution of sulphate of iron is poured carefully upon some sulphuric acid, to which a minute fragment of a nitrate has been added, or upon a cooled mixture of sulphuric acid with a little nitrate solution, a deep greenish-brown halo is produced at the junction of the two liquids, as shown in Fig. 36. This test is also extremely delicate.

ε. **Solution of gold.** Gold leaf when boiled in hydrochloric acid remains unchanged, but upon the addition of a little nitrate becomes dissolved wholly or in part. To demonstrate the solution of the gold in the latter case, protochloride of tin may be added, which will give rise to a purplish precipitate or turbidity.

(116.) In Organic Mixtures.

α. Solid matters should be digested for some time in cold water, and the liquid filtered off. This method is applicable to stains on clothing, when not of too long standing. Viscid and turbid liquids are simply mixed with water and filtered. The suspected filtrate is next tested with blue litmus paper, and if found to be acid, neutralized carefully with a solution of carbonate or hydrate of sodium, evaporated down to the crystallizing point, and set aside. If practi-

cable, the resulting deposit may be collected, dried by pressure between folds of bibulous paper, dissolved in a little warm water, and the solution, filtered, if necessary, evaporated, and recrystallized. Lastly, the crystalline residue is to be examined microscopically, and by the several chemical tests mentioned in the preceding section. The acid reaction may be wanting in organic mixtures, through a neutralization of the nitric acid originally administered.

§ III.—HYDROCHLORIC ACID.

(117.) Concentrated.

α. **Appearance.** The pure solution is colorless, or of a scarcely perceptible greenish tinge; but the commercial acid has frequently a bright yellow color, from the presence of perchloride of iron.

β. **Volatility.** At ordinary temperatures the strong acid evolves colorless, almost transparent fumes, which have a marked acid reaction, a characteristic smell, and, in common with other acid fumes, become opaque upon admixture with ammoniacal vapor. The liquid acid heated on a watch-glass evaporates without leaving any residue.

γ. **Action on organic matter.** Most organic tissues are gradually corroded and tinged of a yellow color by immersion in the strong acid; but the stains produced on black cloth are at first distinctly red, and after some days reddish-brown.

δ. **Want of action on metals.** Hydrochloric acid, boiled with a little copper or mercury, simply evaporates, leaving the metal unchanged, or very nearly so.

ε. **Evolution of chlorine.** Peroxide of manganese, warmed with hydrochloric acid in a test tube, produces an abundant evolution of chlorine gas, recognizable by its greenish-yellow color and irritating

smell. It quickly bleaches litmus paper, and produces a purple coloration on starch paper moistened with iodide of potassium.

(118.) DILUTED.

α. **Neutralization by carbonates, &c.** Dilute hydrochloric acid is completely volatile, has a marked acid reaction, and dissolves most carbonates with effervescence, forming chlorides, which may be obtained in the solid state on evaporation; the alkaline chlorides, and particularly chloride of sodium, crystallizing in cubical or stauroid forms. Chlorine may be liberated from the evaporated residue by the action of sulphuric acid and peroxide of manganese.

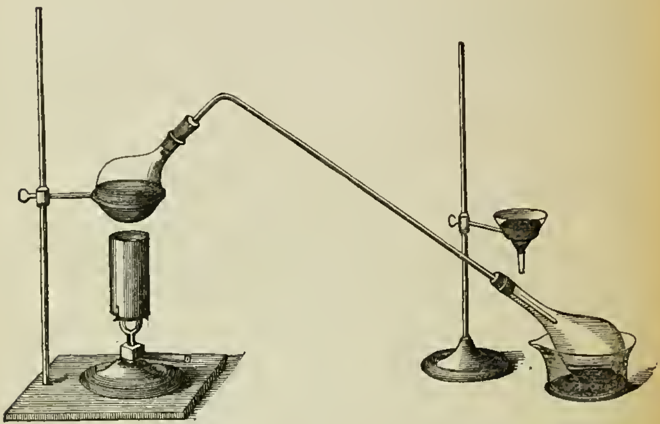
β. **Precipitation of chloride of silver.** Solution of nitrate of silver, added to hydrochloric acid, throws down a white clotty precipitate of chloride of silver, which subsides readily after brisk agitation, and by exposure to light acquires a gray or purplish color. One portion of the precipitate may be treated with ammonia, in which it will dissolve, and another portion boiled with nitric acid, by which it will be unaffected, while the remainder may be washed, dried, and ignited in a porcelain capsule, when it will fuse into a horny mass.

(119.) IN ORGANIC LIQUIDS OR SOLIDS.

α. **Distillation, &c.** The liquid having shown an acid reaction to test paper, may be strained or filtered if necessary, and then distilled nearly to dryness from a retort, or a flask to which a cork and delivery tube have been adapted, as in Fig. 40. The earlier portions of the distillate are usually little else than water, but the later portions should manifest all the properties of dilute hydrochloric acid. Solid substances may be digested in distilled water, and the resulting solution examined with test paper and nitrate of silver. If possible, a portion of the liquid

should be evaporated to thorough dryness, and the dissolved residue again tested with nitrate of silver to ascertain the absence or comparative absence of metallic chlorides.

Fig. 40.



§ IV.—OXALIC ACID.

(120.) Solid.

α. **Appearance, &c.** Oxalic acid generally occurs in colorless, more or less well-defined four-sided prisms, which dissolve readily in boiling water to form a solution having a marked acid reaction.

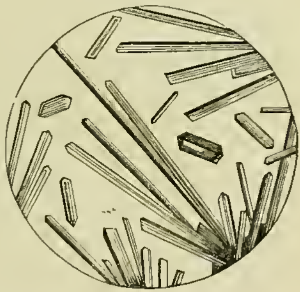
β. **Volatility without charring.** A few crystals of the acid, when heated upon platinum foil, melt, evolve fumes, and disappear without leaving any carbonaceous residue.

γ. **Effervescence with manganese.** A little peroxide of manganese, free from carbonates, when added to oxalic acid moistened with water, sets up an active effervescence of carbonic acid gas.

(121.) DISSOLVED.

α. **Crystalline form.** One or two drops of the strongly acid liquid evaporated cautiously upon a glass plate until a solid white margin appears, yield on spontaneous cooling a crystalline residue of delicate, long flat prisms, as shown in Fig. 41.

Fig. 41.



β. **Precipitation of oxalate of silver.** Nitrate of silver produces in solution of oxalic acid, more abundantly after its neutralization or partial neutralization with ammonia, an opaque white precipitate of oxalate of silver, which is not discolored by ebullition, but may dissolve if the excess of oxalic acid be large, and is readily soluble in dilute nitric acid. The precipitate collected on a filter, washed, dried, and then ignited upon platinum foil, is dissipated with a slight explosion, leaving an inconsiderable pulverulent residue of metallic silver.

γ. **Precipitation of oxalate of calcium.** Solution of sulphate of calcium added freely to aqueous oxalic acid, throws down a white precipitate of oxalate of calcium, insoluble in acetic, but readily soluble in dilute nitric acid. By ignition, the precipitate is converted into carbonate of calcium, which dissolves in acetic acid with effervescence.

(122.) IN ORGANIC LIQUIDS.

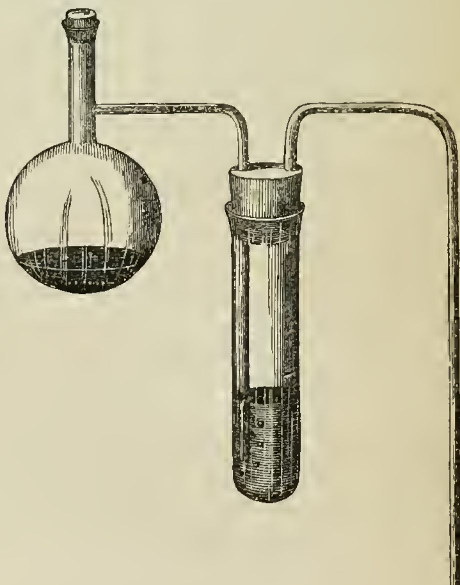
α. **Reaction to test paper, &c.** The acid reaction is very decided even when the poison exists but in very small proportion. It is often necessary to filter the liquid, after previous dilution with water or

proof spirit, or at any rate to strain it through muslin, before applying any reagent.

β. **Precipitation of oxalate of lead.** Solution of acetate of lead added to the strained or filtered liquid, throws down a precipitate of oxalate of lead, either white or discolored by the organic matter present. The addition of the reagent is to be continued until it no longer produces a fresh precipitate. This point is easily ascertained by repeatedly testing the supernatant liquid, which separates readily after briskly agitating the mixture.

γ. **Production of oxalic acid.** The above precipitate of oxalate of lead having been collected on a filter and thoroughly washed, is made into a thin magma with water, and treated with a current of washed sulphuretted hydrogen evolved from some such arrangement as that shown in Figs. 42 and 15,

Fig. 42.



until the mixture, after agitation and standing at rest for a minute or so, smells strongly of the gas; when, with or without previous warming, it is to be thrown on to a filter. The filtrate will be an aqueous solution of oxalic acid, which will yield crystals on evaporation, and manifest all the above-described reactions of the dissolved acid.

δ. **Production of oxalate of ammonium.** Or instead of treating the washed precipitate of oxalate of lead with sulphuretted hydrogen, it may be boiled for a short time with a small quantity of dilute sulphuric acid, the mixture filtered, and the filtrate neutralized with ammonia. The resulting solution of oxalate of ammonium may be concentrated by evaporation and tested with nitrate of silver and sulphate of calcium, when characteristic precipitates of the oxalates of silver and calcium respectively will be obtained.

(123.) Insoluble.

α. Oxalic acid is sometimes met with as a calcium or magnesium salt, owing to the exhibition of chalk or magnesia as an antidote. The insoluble white deposit, when boiled for some time with carbonate of sodium, yields a solution of oxalate of sodium, which after filtration and careful neutralization with dilute nitric acid, may be tested with nitrate of silver and sulphate of calcium respectively. It is recognizable also by effervescing upon treatment with peroxide of manganese and a dilute mineral acid.

§ V.—CORROSIVE SUBLIMATE.

(124.) Solid.

α. **Appearance, solubility, &c.** Corrosive sublimate usually occurs as a heavy, white, glistening powder, turned black by sulphide of ammonium, yellow by potash, and scarlet by iodide of potassium.

Boiled with a little water in a test-tube it undergoes speedy solution.

β. **Volatility.** A small portion of the powder, heated on charcoal or platinum foil, disappears completely with production of opaque white fumes. Heated in a narrow tube it yields a white crystalline sublimate.

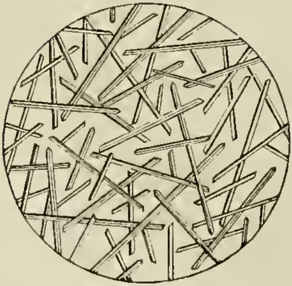
γ. **Metallic reduction.** When a little of the powdered salt, mixed with three or four times its bulk of recently calcined carbonate of sodium, is introduced into a thoroughly dry reduction tube, the mixture covered with some additional carbonate of sodium, and the heat of a spirit or gas-flame applied, first to the carbonate and then to the mixture, volatilization of metallic mercury takes place, and a sublimate of well-defined mercurial globules condenses in the cold part of the tube.

δ. **Detection of chlorine in residue.** The bottom of the tube containing the fused residue having been snapped off at a file-mark and boiled in water, the resulting solution may be acidulated with nitric acid and tested with nitrate of silver, when a white precipitate of chloride of silver will be formed, insoluble in nitric acid, but soluble in ammonia.

(125.) DISSOLVED.

α. **Crystalline form.** A little of the solution evaporated cautiously on a glass plate until a solid margin appears, and set aside to crystallize, furnishes a residue of slender opaque intersecting needles (Fig. 43), which afford the above-described reactions of the solid poison.

Fig. 43.



β. **Precipitation of sulphide of mercury.** Sul-

phuretted hydrogen gas, or its aqueous solution, added to corrosive sublimate solution, produces at first a white turbidity, gradually becoming orange-brown, and finally changing into a dense black precipitate of sulphide of mercury, which may also be thrown down by sulphide of ammonium. The washed precipitate is insoluble even in boiling nitric acid.

γ. **Precipitation of oxide of mercury.** Excess of potash or lime-water produces an orange-yellow precipitate of mercuric oxide, the filtrate from which may be tested for chlorine by means of nitrate of silver and nitric acid.

δ. **Precipitation of iodide of mercury.** Iodide of potassium produces, in corrosive sublimate solution, an orange or scarlet precipitate of iodide of mercury, which disappears in excess of the precipitant, forming a colorless liquid. This reaction is very characteristic, though liable to be interfered with by the presence of various saline compounds.

ε. **Reduction by a stannous salt.** Protochloride of tin, added to a solution of corrosive sublimate acidulated with hydrochloric acid, produces at first a white precipitate of calomel, which, on adding more of the reagent, becomes slate-colored, and finally almost black, from its conversion into metallic mercury. The precipitate subsides rapidly upon the application of heat; afterwards the supernatant liquid may be poured off, replaced by hydrochloric acid, and heat again applied, when the originally bulky deposit will shrink into a few globules of liquid mercury having a highly characteristic aspect.

ζ. **Deposition on copper.** A piece of thin copper foil or gauze immersed in the solution, previously diluted very considerably and acidulated with hydrochloric acid, quickly acquires a silver-like coating of mercury. On heating the washed and dried piece of coated copper in a subliming tube, the mercury volatilizes, yielding a sublimate of metallic globules, while the copper resumes its original red color.

η. **Electrolytic test.** When a few drops of the solution, preferably acidulated with hydrochloric acid, are placed on a sovereign or other piece of gold, and the coin touched through the liquid with a key or other steel instrument, a deposition of mercury takes place upon the gold at the point of contact, forming a silvery stain, which disappears upon the application of heat.

(126.) In Organic Liquids and Solids.

α. **General processes.** The strained or filtered liquid, acidulated with hydrochloric acid and gently warmed, may sometimes be treated with a solution of protochloride of tin, as above described; but the electrolytic test, and especially the test of metallic reduction upon copper, are in most cases much to be preferred. It is generally sufficient to prove the presence of dissolved mercury in an organic liquid, without taking the chlorine of the salt into consideration; but occasionally the entire salt may be extracted by agitating the liquid with ether, evaporating the ethereal solution, and treating the residue with water. Organic solids, thoroughly broken up or otherwise finely divided, are boiled for an hour or so with dilute hydrochloric acid, and the solution tested by immersing in it a piece of clean copper; or, if necessary, the copper may be boiled in the liquid for a considerable length of time.

β. **Special process.** After boiling the broken-up tissue with dilute hydrochloric acid for an hour or so as above described, and filtering off the acid decoction, the undissolved residue should be made into a thin paste with hydrochloric acid diluted with twice its bulk of water, and the mixture heated on a water bath. Then, from time to time, finely powdered chlorate of potassium is to be added little by little until the color of the undissolved substance is reduced to pale yellow tint, when the filtered decoction may be returned, the whole boiled for a few minutes,

allowed to cool, and filtered, the filtrate evaporated to a small bulk, again filtered if necessary, and treated with excess of washed sulphuretted hydrogen gas. The resulting sulphide of mercury, mixed with much sulphur, may be collected on a filter, washed with water, dissolved in hydrochloric acid, to which a minute quantity of chlorate of potassium has been added, the liquid evaporated to dryness, the residue dissolved in water, and the resulting solution of mercuric chloride examined by any of the usual tests. This method is one of general applicability for the detection of metals absorbed into the tissues. The original precipitate produced by sulphuretted hydrogen may in all cases be dissolved in hydrochloric acid, aided by the smallest sufficient quantity of chlorate of potassium as above described, the resulting solution treated afresh with sulphuretted hydrogen, and the precipitate then obtained examined for mercury, lead, copper, arsenic, antimony, bismuth, tin, &c.

§ VI.—LEAD.

(127.) Solid Compounds.

α. **Metallic reduction.** Lead may be readily procured in the metallic state from substances containing it in moderate quantity. When a small portion of any lead compound, mixed with three or four times its weight of carbonate of sodium, is heated on charcoal in the reducing blowpipe flame, a malleable metallic globule is soon produced, while the charcoal receives a yellow incrustation. The globule may be dissolved in dilute nitric acid, and the liquid tests applied to the solution so formed.

β. **Carbonate of lead.** This salt occurs as an opaque white powder, which melts and becomes yellow when heated, is turned black by sulphide of ammonium, is insoluble in water, but dissolves in dilute nitric acid with effervescence, forming a solution to which the liquid tests for lead can be applied.

γ. **Acetate of lead.—Aspect, &c.** Acetate of lead generally occurs as a heavy crystalline powder, of a white color, a peculiar sour smell, and a sweetish astringent taste. It is moderately soluble in distilled water, and forms a milky liquid with common water, containing sulphates or carbonates. Its solution when evaporated upon a glass plate yields opaque white prismatic crystals.

δ. **Acetate of lead.—Reactions.** The salt is turned of a black color by sulphide of ammonium, and of a yellow color by iodide of potassium. When heated in a reduction tube, it melts, resolidifies, becomes dark in color, gives out a smell of acetone, and leaves a carbonaceous residue containing very finely divided metallic lead. When heated in a test tube with sulphuric acid it gives off the smell of acetic acid, convertible into that of acetic ether upon the addition of a little alcohol. Treated with solution of persulphate of iron it yields a white residue of sulphate of lead, and a dark red solution of peracetate of iron.

(128.) DISSOLVED.

α. **Precipitation of sulphide of lead.** Sulphuretted hydrogen gas or its solution in water, when added to any solution containing lead, gives a black or dark brown precipitate of sulphide of lead, insoluble in cold dilute hydrochloric acid, and unaffected by sulphide of ammonium. But in some cases, especially in presence of much chloride of hydrogen or iron, the precipitate comes down of a red color, and is then turned black by sulphide of ammonium.

β. **Precipitation of sulphate of lead:** Dilute sulphuric acid produces an opaque white precipitate of sulphate of lead, insoluble in nitric acid, soluble in boiling and in a large excess of cold hydrochloric acid, and in a considerable excess of potash water. The precipitate is turned black by sulphuretted hydrogen or sulphide of ammonium.

γ. **Precipitation of iodide of lead.** Iodide of potassium added to the lead solution, which should be free from any great excess of free acid or alkali, throws down a bright yellow precipitate of iodide of lead, soluble in hot hydrochloric acid and in a large excess of potash water. It is also sparingly soluble in boiling water, and is reprecipitated on cooling in golden scales.

(129.) IN ORGANIC LIQUIDS OR SOLIDS.

α. **Organic liquids.** The liquid, strained or filtered if necessary, and acidulated with a few drops of nitric or hydrochloric acid, is treated with a current of washed sulphuretted hydrogen, until it acquires a marked smell of the gas, persistent after agitation. The resulting black or dark brown precipitate is allowed to subside, collected on a filter, thoroughly washed with water, and boiled, until its color is destroyed, in nitric acid diluted with about four times its bulk of water. The solution so obtained, filtered if necessary and concentrated by evaporation, is then submitted to the action of the ordinary tests for dissolved lead salts.

β. **Organic solids.** The tissue suspected to contain lead may be treated with hydrochloric acid and chlorate of potassium, as described in par. 116 β. Or it may be dried in an oven, burnt in a capsule, and the resulting charcoal heated to dull redness for several hours until a gray ash is left, which must be dissolved in dilute nitric acid by the aid of heat. The solution of the ash is then to be treated with sulphuretted hydrogen, and the black precipitate further examined.

§ VII.—COPPER.

(130.) DISSOLVED.

α. **Solubility, &c.** Most salts of copper are soluble in water or dilute mineral acids, except the sul-

phide, which, however, dissolves readily in strong nitric acid. The solutions whether aqueous or acidulous have a decidedly blue or green color.

β. **Precipitation of sulphide of copper.** Sulphuretted hydrogen or an alkaline sulphide throws down a dark brown precipitate of sulphide of copper, which is scarcely affected by treatment with cold hydrochloric acid, but dissolves readily in nitric acid, is partly soluble in ordinary sulphide of ammonium, but insoluble in sulphide of sodium or potassium.

γ. **Formation of cuprammonium salt.** Ammonia added carefully to a cupric solution produces a bluish white precipitate, which dissolves in excess of the precipitant, forming a deep purple-blue liquid, of highly characteristic appearance, save when very dilute, in which case it resembles the similarly constituted but strong ammoniacal solution of nickel. It is, however, distinguishable therefrom by means of caustic potash, which, unless added in very large proportion, does not disturb the transparency of the cuprous, but affords a pale green precipitate with the nickel solution.

δ. **Precipitation of ferrocyanide of copper.** Ferrocyanide of potassium produces a gelatinous chocolate precipitate of ferrocyanide of copper, insoluble in mineral acids. Potash changes it into a pale blue magma readily soluble in ammonia, forming a deep blue liquid. By these properties it is distinguished from the similarly colored precipitate of ferrocyanide of uranium. Ferrocyanide of nickel has a pale green color.

ε. **Metallic precipitation on iron.** A steel needle or piece of polished iron wire immersed in a feebly acidulated cupric solution soon acquires a coating of metallic copper, having its characteristic red appearance. When the proportion of copper is very minute, the iron should continue immersed for several hours. Occasionally the deposit is not suffi-

cient in quantity to present the ordinary aspect of metallic copper, but appears simply brown or black.

ζ. **Examination of metallic deposit.** The coated wire, having been washed in water, is acted upon by a drop or two of ammonia when by exposure to air the copper gradually dissolves in the ammonia, forming a deep blue solution, in which, after acidification with acetic acid, ferrocyanide of potassium causes a chocolate red turbidity of ferrocyanide of copper.

η. **Electrolytic test.** When a few drops of an acidulated solution of copper are placed in a platinum capsule, and a piece of zinc foil introduced so as to touch the capsule through the liquid, metallic copper is quickly deposited upon the platinum, either with its characteristic appearance, or simply as a brown stain. The deposit can be examined with ammonia and ferrocyanide of potassium as above described. The process possesses no advantage over that with the iron wire.

(131.) In Organic Liquids and Solids.

α. **Organic liquids.** These, when containing any appreciable quantity of copper, have usually a more or less marked greenish tint. They may be acidulated with hydrochloric acid, and allowed to act upon clean iron wire as above described; or the filtered acidulated solution may be treated with a current of sulphuretted hydrogen gas, and the resulting dark brown precipitate collected upon a filter, washed with water, and dissolved in dilute nitric or in strong hydrochloric acid. The acid solution evaporated nearly to dryness, and diluted with water, can then be examined by the usual tests.

β. **Organic solids.** These, when containing copper even in small quantity, acquire a deep blue color by immersion in ammonia. They may be cut into small pieces, boiled for some time in dilute hydrochloric

acid, and the resulting liquid, after being concentrated by evaporation, examined with a steel needle or a current of sulphuretted hydrogen gas (α). Or the tissue may be destroyed, either with hydrochloric acid and chlorate of potassium, as described in par. 116 β, or by incineration, as described in par. 119 β, and the residues further examined.

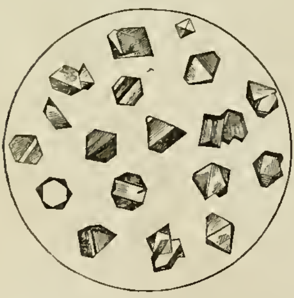
§ VIII.—ARSENIC.

(132.) Arsenious Acid or Anhydride.

α. **Appearance.** Commercial arsenious acid, white arsenic, or arsenious anhydride, usually occurs as a heavy white powder, but may be met with in transparent vitreous masses, or in opaque porcellanous masses, or in masses which are opaque externally and glassy in the centre.

β. **Volatility.** A minute quantity of the powder heated on platinum foil volatilizes entirely with evolution of opaque white fumes; any fixed residue being due to impurity, probably sulphate of calcium. A little of the powder heated in a subliming tube also volatilizes, and deposits an iridescent sublimate in the cool part of the tube. Or the volatilization may be effected in a short wide test tube, and the sublimate condensed on a flat strip of glass held over the mouth of the tube. Upon examination with a lens, the sublimate in the tube or on the glass will be seen to consist chiefly of octahedral crystals, as shown in Fig. 44, which do not polarize.

Fig. 44.



γ. **Action of sulphide of ammonium.** When a drop or so of sulphide of ammonium is added to a little white arsenic contained in a watch glass, there is no alteration of color produced, but on applying a gentle heat, solution takes place, and on evaporating to dryness, a yellow film of sulphide of arsenic is left, soluble in alkalies, insoluble in hydrochloric acid.

δ. **Solubility.** Powdered white arsenic when agitated with water in a test tube, does not perceptibly dissolve, but remains partly as a film over the surface, partly in small aggregations at the bottom. This state of immiscibility, which is very characteristic, does not disappear even on prolonged boiling. By filtration, however, a clear aqueous solution of arsenious acid is obtained. Moreover on adding a little potash or hydrochloric acid to the hot mixture of water and white arsenic, complete solution is very easily effected.

ε. **Reducibility.** A minute quantity of the powder sprinkled upon red-hot charcoal evolves scarcely visible vapors having a peculiar garlic-like odor. When a little white arsenic mixed with three or four times its bulk of dry soda-flux, produced by the incineration of acetate of sodium with some additional charcoal, is introduced into a narrow reduction tube of hard glass, made perfectly dry and warm, there is produced, on subjecting the mixture to the heat of a spirit flame, a sublimate of reduced arsenic which condenses in the upper cool part of the tube in the form of a metallic ring, as shown of the actual size in Fig. 45.

Fig. 45.

Or a minute quantity of white arsenic may be placed in the reduction-tube, covered with a considerable thickness of powdered charcoal, and heat applied from above to below, so that the arsenic may volatilize through the red-hot charcoal, when a ring of reduced metal will appear as before.

ζ. **Characters of the metallic ring.** The arsenical ring is characterized as follows: *a.* By its lustrous steel gray appearance. Should it present an opaque brownish-black color, its proper aspect may be brought out by the cautious application of heat, when the characteristic metallic gray ring will remain, and a more volatile dark-colored compound of arsenic be volatilized. The interior surface of the metallic sublimate, rendered visible by breaking the tube, presents a crystalline appearance. *b.* By its volatility. Upon heating the sublimate to a temperature considerably below redness, it may be readily volatilized from one part of the tube to another. *c.* By its conversion into arsenious anhydride. After repeated volatilizations up and down the tube, the ring of metal is gradually replaced by a ring of iridescent crystals of white arsenic, shown by a lens to consist of variously modified octahedrons. These may be boiled in a small quantity of water for some time, when a solution of arsenious acid will be formed. to which the ordinary liquid reagents can be applied, *d.* By its conversion into arsenic acid. The ring of metal, when warmed with a drop or two of nitro-muriatic acid, disappears, and on evaporating to dryness, a residue of arsenic acid is left, which may be dissolved in water, and tested with nitrate of silver solution, when a brick-red precipitate of arseniate of silver will be produced.

(133.) Dissolved.

α. **Reaction, &c.** The aqueous solution of arsenious acid is clear, colorless, tasteless, inodorous, and has a faintly acid reaction to test-paper. When evapo-

rated upon a glass plate, it leaves a white residue of minute octahedral non-polarizing crystals, which may be volatilized by a further application of heat.

β. **Precipitation of arsenite of silver.** Ammonio-nitrate of silver, added to aqueous arsenious acid, throws down an opaque yellow precipitate of arsenite of silver, soluble in ammonia and in dilute nitric acid. The reagent is made by adding a weak solution of ammonia drop by drop to a strong solution of nitrate of silver, until the brown precipitate at first produced is just redissolved.

γ. **Precipitation of arsenite of copper.** Ammonio-sulphate of copper, added to aqueous arsenious acid, produces a light green precipitate of arsenite of copper, soluble in ammonia and in dilute acids. When collected on a filter, washed, dried, and heated in a reduction tube, it yields a crystalline sublimate of arsenious anhydride. Ammonio-sulphate of copper is made by carefully adding ammonia drop by drop to a somewhat dilute solution of sulphate of copper, until the precipitate at first produced is nearly redissolved.

δ. **Precipitation of trisulphide of arsenic.** When a current of washed sulphuretted hydrogen gas is passed through a solution of arsenious acid acidulated with hydrochloric acid, an abundant bright yellow precipitate of arsenious sulphide or orpiment is produced. Sulphide of ammonium does not give any precipitate with aqueous arsenious acid until some other acid is added; while sulphuretted hydrogen produces only a yellow discoloration.

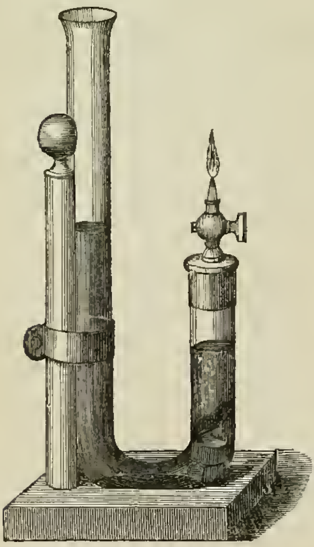
ε. **Characters of the above precipitate.** The yellow precipitate may be collected on a filter, washed with water, and tested as follows. Boiled with hydrochloric acid, it does not perceptibly dissolve, but, on the addition thereto of a little nitric acid, disappears with the formation of red fumes, a globule of melted sulphur frequently remaining undissolved.

Treated with sulphide, hydrate, or carbonate of ammonium, it undergoes solution, and is again thrown down by the addition of hydrochloric acid. Dried and heated in a reduction tube, it sublimes unchanged or nearly so. Dried and heated in a reduction tube, after thorough mixture with four or five times its bulk of soda-flux, it yields a sublimate or ring of reduced metal.

(134.) Marsh's Test.

a. **Nature of process.** When a substance containing arsenic is acted upon by nascent hydrogen, usually developed by the reaction of metallic zinc and dilute sulphuric or hydrochloric acid, a gaseous compound of arsenic and hydrogen, known by the name of arsenetted hydrogen, is given off. This gas may be generated in any ordinary form of hydrogen-apparatus; even the adaptation to one another of a flat-bottomed vial, perforated cork, and piece of glass tube either straight or bent, according to circumstances, and drawn out to a moderately fine point, will answer the purpose. The arrangement shown in Fig. 47 is in some cases very convenient; while in others, the original bent tube devised by Marsh may be most advantageously employed. It may be made quite plain, as in Fig. 46, or be provided with a couple of large strong bulbs, one in the upper part

Fig. 46.



of the long, and one in the lower part of the short limb. This short limb is furnished with a movable stopcock, into which is screwed either a short jet, for burning the issuing gas, as shown in the figure, or an elbow, to which a horizontal piece of glass tubing may be readily adapted. Arsenetted hydrogen is identified by its property of yielding deposits of metallic arsenic, either upon imperfect combustion, as originally pointed out by Marsh, or by exposure to a dull red heat, as recommended by a committee of the French Academy.

(135.) Original Marsh's Process.

When it is intended to obtain deposits by an imperfect combustion of the gas, Marsh's apparatus (Fig. 46) is usually employed in the following manner. The stopcock being removed, a piece of stout glass rod is carefully dropped into the shorter limb of the tube. It should be sufficiently small to reach the bend, but not small enough to pass into the longer limb: a glass stopper will often answer the purpose extremely well. Two or three compact lumps of metallic zinc are then let fall upon the piece of glass, the open stopcock replaced, and cold diluted sulphuric acid, in the proportion of about one part of acid to six or seven of water, poured into the longer limb; so that when the liquid is level in the two limbs, there may yet remain some little free space beneath the stopcock. The dilute acid is allowed to act upon the zinc for a few minutes, and the stopcock then closed, whereby the shorter limb becomes gradually filled with hydrogen gas, the acid being gradually driven up into the longer limb. The stopcock is then opened, and the issuing hydrogen quickly inflamed. It ought to burn with a scarcely visible flame, which should not produce a deposit or even a discoloration upon a piece of clean glass or porcelain momentarily depressed upon it. As soon as all the hydrogen is driven out of the shorter limb by the descending acid,

the stopcock is reclosed while another accumulation of gas takes place, which is then released, inflamed, and examined as before. Or the issuing gas, without being inflamed, may be allowed to impinge on paper moistened with nitrate of silver solution, which should not thereby acquire any discoloration. When, after several examinations, the purity of the hydrogen, and consequently of the materials used to generate it, has been satisfactorily ascertained, the arsenical liquid is introduced and the experiment repeated.

α. **Appearance of flame, &c.** The hydrogen gas subsequently evolved is contaminated to a greater or less extent with arsenetted hydrogen, and produces a metallic-looking discoloration upon paper moistened with nitrate of silver solution. It burns with a bluish flame, and evolves a white smoke of arsenious anhydride.

β. **Reactions of the smoke.** The smoke or vapor may be tested by holding over the summit of the flame a piece of porcelain moistened with ammonio-nitrate of silver, when a yellow turbidity due to arsenite of silver will make its appearance; or by inclosing the flame more than once if necessary by a short wide test-tube moistened on its interior with water, whereby a weak solution of arsenious acid will be formed, which may be tested with sulphuretted hydrogen, or other appropriate reagent.

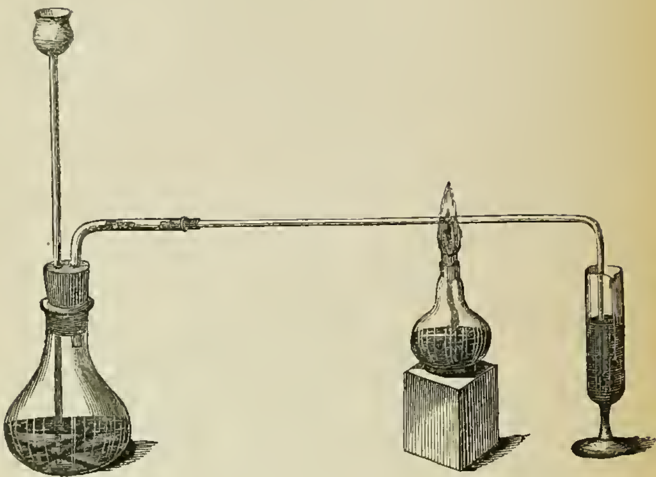
γ. **Formation of deposit.** When a piece of clean glass, porcelain, or talc is momentarily depressed upon the flame so as to cut off about two-thirds of its height, there is produced upon the cold surface a dark stain or deposit which is constituted of three products, in the centre of metallic arsenic, in the exterior of arsenious anhydride, and in the intermediate zone of a compound considered to be a suboxide of arsenic. That the stain is really arsenical is shown by its possessing the following characters: *a.* Metallic brilliancy. The lustrous appearance of the arsenical stain is best seen on its free surface, but is recogniz-

able through the glass. *b.* Hair-brown color. This color appertains particularly to slight stains, and to the intermediate portion of larger stains, in which last it is best manifested by means of transmitted light. *c.* Volatility. The arsenical stain disappears readily on the application of a heat considerably below redness; this property of volatility is very evident when the stain has been produced on a thin plate of talc. During its volatilization the metallic arsenic becomes converted into arsenious anhydride. *d.* Solubility in chloride of lime. When the arsenical stain is warmed with a few drops of bleaching liquid, complete solution speedily takes place. For the application of this test it is convenient to produce the stain on the interior of a watch-glass. *e.* Non-solubility in cold disulphide of ammonium. The arsenical stain is not perceptibly affected by treatment with a drop of yellow sulphide of ammonium solution. But on heating to dryness, a bright yellow stain of orpiment is produced, containing a dark nucleus of undissolved metallic arsenic. (Guy.) *f.* Conversion into arsenic acid. The arsenical stain disappears completely when gently warmed with a drop or two of nitric or nitro-muriatic acid. By evaporating to dryness, a slight residue of arsenic acid is left, recognizable by its ready solubility in a drop of water, so as to form a solution in which nitrate of silver produces a brickdust-red turbidity.

(136.) Modified Marsh's Process.

Marsh's apparatus may also be used for generating arsenetted hydrogen when it is intended to decompose the gas by extraneous heat. In this case the jet of the stopcock is unscrewed and replaced by a metal elbow, to which a horizontal piece of narrow hard glass tubing is adapted. But some such apparatus as that shown in Fig. 47 is on the whole to be preferred. It consists of a small flask furnished with a cork through which passes a long funnel tube,

Fig. 47.



and a short wide rectangular tube, loosely plugged with a little cotton wool, and connected by means of a perforated cork with a long horizontal piece of narrow hard glass-tubing, bent downwards at its extremity so as to dip into a solution of nitrate of silver. The apparatus is charged with pure zinc and dilute sulphuric acid, so as to cause an evolution of hydrogen gas, which passes through the cotton wool, where it deposits any mechanical impurities, along the horizontal tube, and into the silver solution. During the transmission of the gas, the flame of a spirit lamp is applied steadily to some particular part of the horizontal tube, and if after a little time there is not produced any deposit within the tube, or precipitate in the silver solution, the materials are known to be pure, and the arsenical liquid may be introduced.

α. **Decomposition by heat.** The resulting arsenetted hydrogen is decomposed in its passage through the heated portion of the tube, and deposits a steel-gray ring of metallic arsenic at some little distance

beyond the flame. The ring may be identified by its appearance, its position at a little distance beyond the flame, its volatility, its conversion into arsenious anhydride by repeated sublimations, and its conversion into arsenic acid by treatment with nitro-muriatic acid and evaporation to dryness.

β. **Decomposition by nitrate of silver.** Any arsenetted hydrogen that may escape decomposition by the flame, or that may be purposely allowed to escaped, is arrested by the nitrate of silver solution, with formation of a black deposit of metallic silver. On the termination of the experiment, the excess of silver may be precipitated with hydrochloric acid, the filtrate evaporated to dryness, and the residue of arsenic acid dissolved in water and tested with the usual reagents.

(137.) Reinsch's Test.

This test is particularly useful for the detection of arsenic in organic liquids or solids. The suspected liquid is simply acidulated with about one-eighth of its bulk of pure hydrochloric acid, and boiled. The solid tissue is cut up into very small pieces and boiled for some time in a mixture of about one part of hydrochloric acid with six of water.

α. **Deposit on copper.** A small piece of clean copper foil, or preferably of fine gauze, is introduced into the hot acidulated liquid, and the boiling continued for a period varying from a few minutes to a quarter of an hour or longer. Should the copper acquire a gray metallic discoloration, other pieces thereof may be added from time to time, and the supply continued so long as the last added piece assumes any perceptible alteration in color.

β. **Character of deposit.** The pieces of coated foil or gauze are removed from the liquid, washed in water, and dried between folds of bibulous paper. The deposit unless very thick adheres firmly to the

subjacent copper, presents a well-marked metallic lustre, and has a dark steel-gray color, or, if very thin, a somewhat bluish tint. On the application of heat it disappears entirely, while the copper resumes its ordinary appearance.

γ. **Crystalline sublimate.** A piece of the coated copper, held between the fingers, is warmed over a flame, coiled up to a small bulk, and introduced into an ordinary reduction tube (Fig. 45). The heat of a small spirit flame is then carefully applied, at first a little above the coil, and afterwards to the coil itself, whereby the arsenic is volatilized, oxidized, and condensed in the cool part of the tube as a crystalline sublimate. If necessary, several pieces of coated copper may be thus heated successively in the same tube until a sufficiently obvious sublimate of arsenious anhydride is produced, which, when examined by a lens or the low power of a microscope, will exhibit highly iridescent octahedral forms. A small piece of tubing open at both ends, one of which is drawn out to a long, almost capillary, termination, as shown in Fig. 48, is convenient for volatilizing a very slight

Fig. 48.

deposit. The coated foil having been introduced and tilted down to the shoulder the tube is sealed by the blowpipe at the point *a*, and the resulting cylindrical bulb containing the foil heated in a spirit-flame, from its capillary shoulder backwards to its sealed extremity, whereby a crystallized ring becomes condensed in the capillary projection at *b*.

δ. **Reactions of the sublimate.** By means of a couple of file-marks, the short length of tubing containing the sublimate may be broken off from the two ends of the tube, and the sublimate itself be

acted upon by reagents. Moistened with sulphide of ammonium solution and dried in a water-bath, it yields a yellow residue of orpiment. Moistened with a mixture of nitric and a little hydrochloric acid and evaporated to dryness, it leaves a slight residue of arsenic acid, which produces a red turbidity when treated with a drop of nitrate of silver solution.

(138.) Impediments to Reinsch's Test.

α. **Influence of oxygenants.** Reinsch's process is not applicable in the presence of oxidizing bodies, which moreover enable dilute hydrochloric acid to dissolve metallic copper. But the majority of such compounds may be reduced by the action of sulphite of sodium upon the acidified liquid, while any excess of sulphurous acid from the decomposition of the salt may be got rid of by ebullition before introducing the foil or gauze.

β. **Purity of the acid.** This may be ascertained by diluting a sufficient quantity of the hydrochloric acid with about four times its bulk of water, and boiling a very small piece of foil or gauze in the diluted liquid for a period of twenty minutes or half an hour.

γ. **Purity of the copper.** As even in the most satisfactory performance of Reinsch's test, there is always some, although but an extremely minute quantity of the copper dissolved, and as commercial copper is rarely quite free from arsenic, it is important that the foil or gauze employed in the experiment should be specially tested as to its purity. If, however, the solution of four or five grains of the copper does not yield any evidence of arsenic, the metal is quite pure enough for the purpose, even though a trace of arsenic should be detected in a larger quantity of it. A few grains of the copper cut into fine pieces are placed in a small tube-retort, or in a bulb-tube, such as that shown in Fig. 14, with

not less than twice their weight of precipitated peroxide of iron, and an excess of hydrochloric acid. The mixture is then distilled to dryness, great care being taken at the last to prevent spurting. Any arsenic orginally contained in the copper is in this manner carried over in the form of chloride of arsenic, and may be condensed in a little water with the excess of aqueous hydrochloric acid. The resulting liquid may then be tested for the presence of arsenic by boiling in it a fresh piece of clean copper gauze or foil.

δ. **Modified processes.** The peroxide of iron mentioned above may be replaced by an equivalent quantity of perchloride of iron. Indeed it is better to dissolve the peroxide in excess of hydrochloric acid, and then employ the residue left on evaporating to dryness, which will be free from any trace of arsenic the peroxide itself may have originally contained. Moreover, oxide or chloride of copper may be substituted for the peroxide or perchloride of iron, though not with advantage. Or the copper may be dissolved in hydrochloric acid alone, without the addition of any special oxygenant, by moistening the metal with the acid and exposing both to the air for several days. The addition of a few drops of a solution of perchloride of iron or chloride of copper to the acid greatly facilitates this solution by exposure to air. The hydrochloric solution, no matter how obtained, is eventually distilled to dryness, and the distillate tested for arsenic.

(139.) Other Forms of Arsenic.

α. **Orpiment** and **realgar.** These sulphides of arsenic are yellow or orange-colored compounds, which volatilize unchanged upon the application of heat. Mixed with soda flux and heated in reduction tubes, they give rise to sublimates of metallic arsenic; and the residues, when moistened with hydrochloric acid, evolve sulphuretted hydrogen, recognizable by

its smell and action on lead paper. Orpiment and realgar are not dissolved by boiling hydrochloric acid, but disappear more or less completely in nitro-hydrochloric acid, forming solutions from which arsenic acid may be obtained by evaporating to dryness. They also dissolve in sulphide of ammonium, and are redeposited on evaporating the liquid to dryness.

β. **Scheele's green.** This well-known green pigment is an impure arsenite of copper. Heated in a reduction tube, it yields a crystalline sublimate of arsenious anhydride, and a black residue of oxide of copper, which may be dissolved in hydrochloric acid, and tested by the usual reagents. Arsenite of copper dissolves in dilute hydrochloric acid, forming a solution in which, after precipitation of the copper by excess of oxalate of ammonium, arsenic may be detected by sulphuretted hydrogen, or by Marsh's or Reinsch's tests.

(140.) In Organic Mixtures.

α. A hydrochloric acid decoction may be prepared as already described and tested by Reinsch's process. Or the organic substance may be distilled to dryness with hydrochloric acid, the residue redistilled with fresh hydrochloric acid, the two distillates collected in water, and the product examined by sulphuretted hydrogen, or by Marsh's or Reinsch's process. Or the tissue, &c., may be destroyed with hydrochloric acid and chlorate of potassium, the solution submitted to the prolonged action of sulphuretted hydrogen, and the resulting precipitate further examined (*vide* par. 116 β).

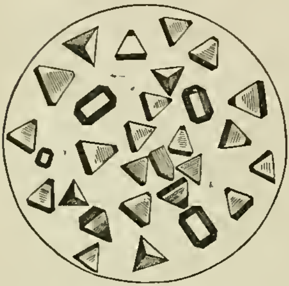
§ IX.—ANTIMONY.

(141.) Antimonial Salts.

α. **Tartar emetic.** This compound usually occurs as a white powder, or in ill-defined crystalline masses

It becomes charred by heat, and when ignited with a little carbonate of sodium on charcoal before the blowpipe, yields a bead of brittle metal and an abundant white incrustation. It is turned of an orange color, and finally dissolved by sulphide of ammonium. Its solution in water when carefully evaporated yields beautifully polarizing crystals (Fig. 49), chiefly tetrahedral, but here and there cubical and octahedral. When acidified by nitric or hydrochloric acid, it furnishes a white precipitate soluble in excess of either acid.

Fig. 49.



β. **Chloride of antimony.** This is a highly corrosive fuming liquid, usually having a yellow or orange color from the presence of chloride of iron. Poured into water, it gives rise to an abundant white precipitate, which after thorough washing with water, is turned of an orange color and finally dissolved by sulphide of ammonium. The precipitate is also readily soluble in tartaric acid. Mixed with carbonate of sodium and heated on charcoal before the blowpipe, it yields a bead of brittle metal and an abundant white incrustation.

(142.) In Solution.

α. **Precipitation of trisulphide of antimony.** A current of sulphuretted hydrogen gas passed into an antimonial solution acidified with tartaric acid, throws down an orange precipitate, which after washing with water, is insoluble in carbonate, but soluble in sulphide of ammonium, forming a solution from which it may be reprecipitated on the addition of an acid.

β. **Precipitation of oxichloride of antimony.** Precipitated trisulphide of antimony dissolves completely in hot hydrochloric acid with evolution of sulphuretted hydrogen gas. The resulting trichloride of antimony, freed from excess of hydrochloric acid by evaporation to a small bulk, gives when poured into water an abundant white precipitate of oxichloride of antimony, soluble in tartaric acid.

γ. **Metallic precipitation on tin.** A piece of tinfoil or bar immersed in the above tartaric acid solution, becomes speedily covered with a pulverulent black deposit of metallic antimony.

(143.) Marsh's Test.

The antimonial solution, acidulated with tartaric acid, may be introduced into the original or modified form of Marsh's apparatus, previously charged with pure zinc and dilute sulphuric acid, and the resulting gas examined as follows:—

α. **Appearance of flame, &c.** Hydrogen contaminated with antimonetted hydrogen produces a black discoloration on paper moistened with nitrate of silver solution. It burns with an opaque bluish white flame, and evolves a white smoke of teroxide of antimony, which, unlike the arsenical smoke, does not produce a yellow turbidity with ammonio-nitrate of silver.

β. **Characters of deposit.** When a piece of talc, porcelain, or glass is depressed upon the flame, a dark stain or deposit is produced, distinguishable from the arsenical stain by the following properties: *a*, by its comparative want of metallic lustre; *b*, by its smoky black color; *c*, by its non-volatility save at a heat approaching redness; *d*, by its insolubility in chloride of lime; *e*, by its ready solubility in yellow sulphide of ammonium, so as to form a solution which on evaporation to dryness leaves a bright orange stain; and *f*, by its yielding after treatment with nitro-mu-

riatic acid and evaporation to dryness, a residue which does not give a red precipitate with nitrate of silver solution.

γ. **Decomposition by heat.** Instead of burning the antimonetted hydrogen, it may be transmitted through a tube heated to redness, and finally through a solution of nitrate of silver. The deposit of antimony produced in the tube is characterized by its position, just before and beyond the exact spot where the heat is applied, by its want of volatility, by its non-convertibility into arsenious anhydride or arsenic acid, and by its ready solubility in yellow sulphide of ammonium to form a solution which leaves a bright orange stain on evaporation.

δ. **Reaction with nitrate of silver.** Antimonetted hydrogen produces in nitrate of silver solution a black deposit of antimonide of silver, from which, after washing with water, the antimony may be dissolved away by a boiling solution of cream of tartar, and precipitated from the resulting solution by sulphuretted hydrogen.

(144.) Reinsch's Test.

α. **Deposit on copper.** The deposition of antimony upon copper foil or gauze boiled in a hydrochloric acid decoction of organic matter contaminated with antimony, or in a weak acidulated solution of some antimonial salt, takes place exactly as does the deposition of arsenic under similar circumstances. The highly lustrous deposit of antimony differs from that of arsenic in having a marked violet color, and in being less easily dissipated by heat. When a piece of the coated foil or gauze is strongly heated in a reduction tube, it either does not afford any sublimate at all, or else a very slight white deposit situated close to the heated end of the tube, not having a crystalline character, and being practically non-volatile.

β. **Solution of deposit.** When boiled for a few minutes in a weak feebly alkaline solution of permanganate of potassium, the antimonial coating is dissolved away from the copper, while the permanganate loses its color and furnishes a slight turbidity of manganic hydrate. The filtered liquid acidulated with hydrochloric acid and treated with sulphuretted hydrogen, acquires a yellowish color, and on standing deposits an orange precipitate, which may be further examined if necessary. Or, if the antimonial coating be not very thick, it will suffice to boil the copper for some time, with frequent exposure of its surface to the air, in a weak solution of caustic potash only, and to treat the resulting liquid, after acidification by hydrochloric acid, with sulphuretted hydrogen.

(145.) In Organic Mixtures.

The processes of precipitation by sulphuretted hydrogen and deposition on copper are perfectly applicable to acidified organic liquids, and to the hydrochloric acid decoctions of organic tissues. Or the tissue may be destroyed by hydrochloric acid and chlorate of potassium, the solution after evaporation treated by sulphuretted hydrogen, the resulting precipitate dissolved in boiling hydrochloric acid, and the solution so formed tested in Marsh's apparatus, or by the process of Reinsch.

§ X.—PRUSSIC ACID.

(146.) In Aqueous Solution.

α. **Appearance, &c.** Prussic or hydrocyanic acid CNH occurs in the state of aqueous solution as a colorless, perfectly volatile, feebly acid, mobile liquid. Its vapor, which is given off at all ordinary temperatures, is invisible, has an odor said to be like that of bitter almonds, and when inspired even in minute quantity causes a peculiar sensation in the fauces.

β. **Formation of Prussian blue.** The turbid greenish liquid made by adding excess of potash to solution of ordinary sulphate of iron, does not undergo any visible alteration when mixed with aqueous prussic acid; but, on acidifying the mixture with hydrochloric acid, a bright blue, or sometimes a greenish-blue color is developed, due to the production of finely divided Prussian blue, which gradually separates as a distinct precipitate. Or the potash and sulphate of iron may be added separately to the suspected liquid, and the mixture be afterwards acidulated with hydrochloric acid.

γ. **Formation of sulphocyanate of iron.** Aqueous prussic acid, mixed with a drop or two of yellow sulphide of ammonium solution, and evaporated to dryness at a low temperature, leaves a residue of sulphocyanate of ammonium, which when moistened with water and tested with a drop of perchloride of iron, produces a dark-red solution of persulphocyanate of iron.

δ. **Formation of cyanide of silver.** Solution of nitrate of silver added to aqueous prussic acid throws down a white precipitate of cyanide of silver, which quickly subsides after agitation. It is not affected by cold nitric acid, but when separated from the supernatant liquid dissolves more or less completely in the strong boiling acid. The precipitate collected on a filter, washed, dried, and heated in a reduction tube, evolves cyanogen gas, which, if ignited at the mouth of the tube, will burn with its peculiar rose colored flame.

ε. **Decompositions of precipitate.** The precipitate treated with hydrochloric acid evolves prussic acid vapor, which may be received on the interior of a watch-glass moistened either with yellow sulphide of ammonium, or with a mixture of potash and sulphate of iron, as described under the head of the vapor reactions. Or a portion of the precipitate

may be treated with a drop of yellow sulphide of ammonium, dried at a low temperature, and the residue, after being moistened with water, tested by a drop of perchloride of iron, when a dark-red liquid will be produced, easily distinguishable from the black precipitate of sulphide of silver. Or a portion of the precipitate may be treated first with potash, then with a drop of sulphate of iron, and lastly with a little hydrochloric acid, when Prussian blue will be formed, together with white chloride of silver.

(147.) In Vaporous State.

The succeeding tests may be applied to the vapor of the pure liquid acid, or to the vapor produced by the action of hydrochloric acid upon precipitated cyanide of silver, or to the vapor evolved spontaneously from organic liquids or solids containing prussic acid. Organic substances which do not react satisfactorily with these vapor tests may be distilled in a water-bath, and the distillate treated similarly to the pure aqueous acid as above described.

α. **Formation of Prussian blue.** When a mixture of potash and sulphate of iron, smeared upon the interior of a watch-glass, or preferably on a flat glass slip (Fig. 50), is exposed for a few minutes to the action of prussic acid vapor, there is produced on acidification with hydrochloric acid, a solution of the iron magma and development of Prussian blue.

Fig. 50.

β. **Formation of sulphocyanate of iron.** A drop of yellow sulphide of ammonium placed on a watch-glass or glass slip and exposed for a short time to the action of prussic acid vapor, yields, when evaporated to dryness at a low temperature, a residue of sulphocyanate of ammonium,

which produces a dark red color, on the addition of perchloride of iron.

γ. **Formation of cyanide of silver.** A drop of nitrate of silver, placed on a watch-glass or glass slip and exposed to the action of the vapor, becomes white and opaque from the formation of cyanide of silver, convertible into Prussia blue, or sulphocyanate of iron, as previously described.

When the prussic acid vapor from some organic mixture is contaminated with sulphuretted hydrogen, it produces a blackening of the silver salt; but no interference with the sulphocyanate reaction is manifested under the same circumstances.

§ XI.—STRYCHNIA.

(148.) In Pure Salt.

α. **Nature, solubility, &c.** Strychnia is a vegetable alkaloid, having the formula $C_{21}H_{22}N_2O_2$. It is more or less freely soluble in alcohol, chloroform, benzole and ether; scarcely at all soluble in pure water; but readily soluble in acidulated water. It is capable of uniting with and neutralizing acids, to form definite crystallizable salts, of which the sulphate, nitrate, hydrochlorate, oxalate, tartrate, and acetate are soluble in water. Most other strychnia compounds are more or less insoluble, whence solutions of strychnia salts are precipitated by a very great number of reagents, including hydrate, carbonate, iodide, sulphocyanate and chromate of potassium, carbazotic acid, phospho-molybdate of sodium, iodide of potassium with iodine, potash double iodide of mercury and potassium, perchloride of platinum, trichloride of gold, &c.

β. **Appearance.** Strychnia usually occurs in the form of a crystalline powder, or of well-defined prismatic crystals, either white, or of a pale buff color. The ordinary salts of strychnia are generally met with as crystalline powders. Strychnia and its salts when

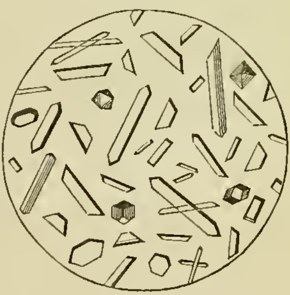
heated, melt, burn with a smoky flame, and leave a carbonaceous residue.

γ. **Bitter taste.** The bitterness of strychnia is peculiar, and has been sometimes spoken of as metallic. Its intensity is so great, that one drop of a gallon of water, in which a grain of strychnia is dissolved, presents a recognizable bitter taste; while with $\frac{1}{10000}$ part of strychnia in solution, the bitterness is well marked and persistent. The taste of strychnia salts is but slightly less intense than that of the alkaloid itself. In very dilute solutions only is the bitterness capable of partial concealment by other sapid bodies.

δ. **Crystalline form.** A drop or so of a spirituous or ethereal solution of strychnia allowed to evaporate spontaneously on a glass slip, furnishes a crystalline residue consisting of rectangular prisms often terminated by double or single oblique planes, and in variously modified octahedra, as shown in Fig. 51. The forms deposited from a chloroformic solution are, for the most part, not well characterized.

ε. **Precipitation.** Aqueous solutions of strychnia salts, containing from $\frac{1}{1000}$ to $\frac{1}{500}$ part of strychnia, are precipitated by the several reagents mentioned either immediately or on stirring; the most delicate though least characteristic precipitants being the phospho-molybdate of sodium, and the potash solution of hydrargyro-iodide of potassium. Hydrate or carbonate of potassium causes a gradual deposition of well defined strychnia crystals, insoluble in excess of the precipitant (Fig. 51). The precipitates thrown down by iodide, sulphocyanate, and chromate of potassium, carbazotic acid, and the chlorides of platinum and gold, are also crystalline.

Fig. 51.



ζ. **Action of acids.** Strong sulphuric acid is without action on strychnia, even at and above the temperature of boiling water. Strong nitric acid usually produces a yellow, or yellow-brown, discoloration; but is said to be without visible action on perfectly pure strychnia, although this seems doubtful.

η. **Color tests.** When a little peroxide of lead is added to a fragment of strychnia, dissolved in a drop of strong sulphuric acid mixed with $\frac{1}{4}$ of its bulk of strong nitric acid; or preferably, when a little peroxide of manganese, or bichromate, or ferridcyanide, or permanganate of potassium, is added to a fragment of strychnia dissolved in a drop of strong sulphuric acid, there is produced a magnificent purple-blue color, becoming gradually crimson, and finally reddish pink. The delicacy of this test, when special precautions are taken, is almost illimitable, less than $\frac{1}{1000000}$ of a grain having been stated to give the reaction. With from $\frac{1}{5000}$ to $\frac{1}{10000}$ of a grain it is easily obtainable. In operating on small quantities, the following plan may be adopted with advantage. The dry strychnia, usually the residue of an evaporation, in which case it must be allowed to become quite cold, is moistened with the smallest sufficient quantity of strong sulphuric acid. By the side of it is next placed a minute drop of a mixture of sulphuric acid with a little very finely-powdered amorphous peroxide of manganese, and the two then brought into contact. The experiment should be made on a surface of white porcelain, or on a flat watch-glass or glass slip, resting on a sheet of white paper.

θ. **Physiological test.** When a minute quantity of solid or dissolved strychnia is introduced underneath the incised skin of a small frog, well-marked tetanic convulsions are manifested by the animal, usually within a quarter of an hour; and with a strong dose almost immediately. This tetanus is said to have been produced with so small a quantity as $\frac{1}{5000}$ of a grain of strychnia; but the delicacy of the

test varies much with the state of the animal, fresh-caught young frogs being the most excitable.

(149.) In Organic Mixtures.

a. If a liquid, it is merely acidified, mixed in some cases with a little spirit of wine, filtered, evaporated nearly to dryness, and the residue extracted with strong alcohol. If a solid, it is brought into a state of fine division, and mixed with a little proof spirit acidulated with dilute sulphuric or other acid, acetic, oxalic, tartaric, &c. After digestion for some time in a water bath, the mixture is filtered, the insoluble matters washed with proof spirit, the washings added to the filtrate, the whole of the clear liquid evaporated down to a small bulk, and the residue so obtained extracted with strong alcohol. The alcoholic solution is then evaporated to dryness, the residue dissolved in a little water, the liquid filtered into a long tube or bottle, and rendered alkaline with carbonate of potassium. Two or three times its volume of ether are next added, and the whole shaken up briskly for some time. After subsidence, the ethereal solution is poured off, and allowed to evaporate spontaneously, whereby a residue is left of more or less well crystallized strychnia. This may be further purified by moistening it with strong sulphuric acid, and heating it for some time in a water bath, then diluting with water, supersaturating the acid liquid with potash, again extracting with ether, and evaporating. The final product may be examined under the microscope, by the color and physiological tests, and by the tongue. In the above process, chloroform or benzole may be substituted for the ether.

§ XII.—MORPHIA.

(150.) In Pure State.

a. **Nature, solubility, &c.** Morphia is a vegetable alkaloid, having the formula $C_{17}O_{19}NO_3$. It

neutralizes acids to form salts, one of which, the meconate of morphia, exists largely in opium, and is the source from which the alkaloid is obtained. Morphia is readily soluble in hot, less so in cold alcohol, very sparingly soluble in ether, and almost insoluble in water, save in the presence of acids. Its ordinary salts dissolve readily in water to form solutions, which are precipitable by a great number of reagents, including most of those which precipitate strychnia. Solutions of morphia and its salts have a well-marked bitter taste.

β. **Appearance, &c.** Morphia is usually met with in the state of acetate or hydrochlorate, which salts sometimes occur finely crystallized, but more often as imperfectly crystalline powders of a buff-tinted white color. The alkaloid itself occurs in quadrangular prisms, frequently having two opposite edges truncated so as to produce hexagonal forms. Morphia and its salts when heated, melt, burn with a smoky flame, and leave a carbonaceous residue.

γ. **Crystalline form.** Morphia, when deposited by the spontaneous evaporation of its alcoholic or ethereal solution, or when slowly precipitated by caustic or carbonated alkalies from aqueous solutions of its salts, occurs in the form of variously modified prismatic crystals, as shown in Fig. 52.

Fig. 52.

δ. **Precipitation by potash.** A single drop of potash added to the somewhat concentrated solution of a morphia salt, produces after some time, or on brisk stirring, a white precipitate of morphia, very soluble in excess of the precipitant, but reproducible by an absorption of carbonic acid from the air.

ε. **Coloration by nitric acid.** Strong colorless nitric acid added, in considerable quantity, to the cold solution of a morphia salt, produces a deep orange-red coloration. Or a drop or two of the acid may be added to a little powdered morphia or morphia salt, on a watch-glass or capsule, when an intense coloration will be at once developed. But the behavior is not peculiar to morphia.

ζ. **Coloration by a persalt of iron.** A drop or two of a carefully neutralized solution of perchloride of iron, added to a morphia solution, or to the dry alkaloid or salt, produces a deep blue color, rendered bluish green by any excess of the iron solution.

η. **Decomposition of iodic acid.** A few drops of aqueous iodic acid produce, in solutions of morphia, a brown discoloration, only in part due to the liberation of iodine. Ammonia, added after a little while, deepens the color considerably. A piece of starched paper, dipped into the colored liquid before it has been treated with ammonia, acquires a purple color, save when the quantity of the alkaloid is very small.

θ. **Reduction of bichromate of potassium.** Strong sulphuric acid produces no coloration with morphia salts or solutions. But a little bichromate of potassium solution dropped carefully on to the sulphuric acid mixture is quickly reduced with production of a bright green color.

(151.) Opiate Liquids.

In the examination of liquids supposed to contain opium, the presence of both morphia and meconic acid is usually sought for. The last named body is not indeed poisonous, but is characteristic of opium, and possessed of well-marked properties.

α. **Preliminary test for morphia with nitric acid.** Strong nitric acid, added in considerable

quantity to an opiate liquid, will often produce a very perceptible darkening or even a distinct orange-red coloration. If necessary, the original liquid may have its color reduced by moderate dilution with water before the addition of the acid.

β. **Preliminary test for meconic acid with perchloride of iron.** To the opiate solution reduced to a pale color by dilution with even a very large proportion of water, a few drops of perchloride of iron are added, when, if meconic acid be present even in small quantity, a distinct reddening of the liquid will be produced.

γ. **Precipitation of meconate of lead.** The opiate liquid acidulated with acetic acid is treated with acetate of lead, so long as a precipitate continues to be produced, when the whole is well agitated, and after partial subsidence thrown upon a wet filter. Meconate of lead remains as an insoluble deposit on the paper, while the filtrate contains acetate of morphia, together with the excess of acetate of lead.

δ. **Production of meconic acid from precipitate.** The precipitate having been thoroughly washed with water, is boiled for some minutes with a small quantity of dilute sulphuric acid, and the mixture thrown upon a filter, whereby a solution of meconic acid is obtained. Or the washed precipitate suspended in a little water may be treated with excess of sulphuretted hydrogen gas, and the clear liquid filtered off, and gently evaporated.

ε. **Test for meconic acid by persalt of iron.** The filtrate produced by either of the above means is then tested with a few drops of perchloride of iron, which should produce a dark logwood red color, through the formation of meconite of iron. The red liquid does not alter its color on boiling, in which respect it differs from the similarly colored solution of peracetate of iron, neither is it bleached by treatment with corrosive sublimate, in which respect it differs

from the similarly colored solution of sulphocyanate of iron.

ζ. **Separation of morphia.** Through the liquid filtered from the precipitate of meconate of lead, but having more or less acctate of lead in solution, a current of washed sulphuretted hydrogen is passed, until the smell of the gas is persistent even after agitation, when the whole is thrown upon a filter. The clear filtrate containing acetate of morphia is evaporated down to a small bulk, supersaturated with carbonate of potassium, and agitated with an ethereal solution of acetic ether. After subsidence, the ethereal solution is poured off and allowed to evaporate spontaneously, when there is left a residue of morphia in more or less well-defined crystals, to which the several tests for the alkaloid can be successfully applied.

CHAPTER IV.

ANIMAL CHEMISTRY.

§ I.—COMPOSITION OF TISSUES, &c.

(152.) Organic and Mineral Constituents.

a. The animal fluids and tissues consist of water together with a certain amount of solid matter. When an animal tissue or fluid is kept for some time at, or a little above, the temperature of boiling water, its aqueous portion evaporates off more or less completely, leaving the dry solids behind. This residuum, when heated upon platinum foil, undergoes combustion; some of its constituents are dissipated, and a black carbonaceous mass remains. If this carbonaceous residue be further heated for some time, especially in a current of air, the black color will gradually disappear, and a white ash, fusible or infusible according to circumstances, will be left upon the foil. The components of dried animal matter are thus separated into two classes; one comprising the substances which are destroyed by fire, and which are called the organic constituents; the other comprising the substances which resist the action of fire, and which are called the inorganic constituents, or more simply the ashes. This distinction, however, is not absolute.

The organic components of animal matter consists principally of—

CARBON.	NITROGEN.
HYDROGEN.	SULPHUR and
OXYGEN.	PHOSPHORUS.

These are also called the elementary or *ultimate* principles of organic bodies.

The ashes consist principally of—

SODIUM.	SULPHURIC ACID.
POTASSIUM.	PHOSPHORIC ACID.
CALCIUM.	CARBONIC ACID.
MAGNESIUM.	CHLORINE.
IRON.	FLUORINE.

Nearly all animal products are composed of both organic and inorganic constituents. Some few substances, however, pertain almost entirely to one class: thus, while the enamel of the teeth contains scarcely any organic matter, some of the crystals of uric acid met with in the urine affords scarcely any ash.

In animal tissues or fluids, the ultimate organic elements are combined with one another in a variety of ways, constituting definite compounds, which are known as *proximate* organic principles: thus in urine we may have all the above-mentioned ultimate principles united with one another, to form the proximate principles, urea, uric acid, sugar, albumen, &c.

The muscular tissue is a very suitable material to be employed for the demonstration of the principal organic and mineral constituents of animal bodies: the same general plan is adopted in other instances.

(153.) ULTIMATE ORGANIC CONSTITUENTS.

a. **Desiccation.** The flesh or other tissue is cut into small pieces and dried in a water bath until it ceases to lose weight. By this means it is divided into an aqueous portion which has evaporated, and a solid portion which remains. Nearly all animal matters behave in a similar way; but nitrogenous substances having an alkaline reaction, give off water containing a variable amount of ammonia.

β. **Destructive distillation.** A few fragments of the dried flesh are placed in a reduction tube, into the mouth of which are inserted a narrow strip of red litmus paper, and a similar strip of lead paper. On applying the heat of a spirit-lamp, water will condense in the upper part of the tube, proving the presence of **oxygen** and **hydrogen** in the flesh—a smell of ammonia will be given off, and the litmus paper become blue, results indicating the presence of **nitrogen**—the lead paper will become blackened, showing the presence of **sulphur**—and lastly, black mass consisting chiefly of **carbon** will remain in the tube.

γ. **Incineration.** If some of the dried flesh be heated upon a piece of platinum foil, or in a shallow capsule, it will swell up, burn with a smoky flame, and leave an abundant carbonaceous residue. On continuing the application of heat for some time, the carbon will gradually burn away. Its disappearance may be facilitated by occasionally pulverizing the coherent residue resulting from the ignition. Throughout the process the temperature should not exceed, or indeed scarcely arrive at, a full red heat. As soon as a pale gray or ochry red ash is produced, the heating may be discontinued.

δ. **Detection of nitrogen.** A little of the finely divided dry substance is intimately mixed ten or twelve times its bulk of soda-lime (made by slacking quicklime with caustic soda solution) and the mixture heated in a reduction tube, whereby ammonia is given off, recognizable by its smell and reaction on test-paper.

ε. **Detection of sulphur.** Bodies of a moderately light color may be tested for sulphur by boiling them in aqueous potash, to which solution of acetate of lead has been added in quantity insufficient to render the liquid permanently opaque. Should the substance so treated contain sulphur it will become stained of a brown or black color, which cannot be removed by

subsequent washing with water. If a substance is stained in the above manner when boiled in a potash solution of lead, and is scarcely or not at all deepened in color when boiled in a solution of pure potash (free from lead), the presence of sulphur is certain. In the case of bodies readily soluble in potash water, the results are not quite so characteristic.

ζ. **Deflagration with nitre.** A little of the dried and finely divided animal matter is mixed with about an equal bulk of powdered nitre, and the mixture projected in small portions at a time into a porcelain crucible kept at a red heat. Deflagration immediately takes place, and, in the fused residue, the presence of carbonic, sulphuric, and phosphoric acids, resulting from the oxidation of carbon, sulphur, and phosphorus respectively, may be ascertained by the usual tests.

In performing the above experiments, very different results will be obtained with different substances, such, for instance, as pieces of flannel, hard white of egg, refined gelatine, sugar, fat, &c.

(154.) Ash of Animal Matter.

α. A small portion of the ash, resulting from the incineration of any kind of animal matter, is placed on a watch-glass, moistened with water and examined by test-papers. Should it not have an acid reaction, a drop or so of nitric acid is to be added, and any effervescence due to **carbonic acid** carefully noted. The remainder of the ash is boiled in a small quantity of water for some time, a few drops of carbonate of ammonium solution added, the whole thrown upon a filter, and the filtrate set aside for examination. The residue is then well washed with water, boiled in a little hydrochloric acid with which a few drops of nitric acid have been mixed, the liquid evaporated just to dryness, diluted with water, and filtered. In

this manner an aqueous and an acidulous solution are obtained, containing respectively:—

Aqueous Solution.	Acid Solution.
POTASSIUM.	IRON PEROXIDE.
SODIUM.	CALCIUM.
SULPHATES.	MAGNESIUM.
CHLORIDES.	PHOSPHATES.
PHOSPHATES.	

β. **Treatment of acid solution.** A little of this solution may be examined for **phosphoric acid** by molybdate of ammonium (par. 100 δ.), and another portion tested for **iron** by ferrocyanide or sulphocyanate of potassium (par. 77). To the remainder of the solution acetate of ammonium is added, and, in the event of there being no decided reddening produced, a little perchloride of iron also. The whole is then boiled for some time, whereby a red precipitate of basic **phosphate of iron** is thrown down, the deposition of which may sometimes be facilitated by the careful addition of ammonia in quantity not sufficient to produce neutrality. The boiling liquid is next filtered, whereby a clear colorless solution should be obtained, perfectly free from both iron and phosphoric acid. Excess of oxalate of ammonium added to this solution throws down a precipitate of oxalate of **calcium.** The resulting turbid mixture, having been well shaken or stirred, is set aside for a little while, and, after partial subsidence, passed once or twice through filtering paper, when **magnesium** may be tested for in the clear liquid by means of ammonia and phosphate of ammonium.

γ. **Treatment of aqueous solution.** Separate portions of this solution, acidified with nitric acid, may be tested for **sulphates** by chloride or nitrate of barium (par. 95 α.); for **chlorides,** by nitrate of silver (par. 96 α.); and for **phosphates,** by molybdate of ammonium, or by sulphate of magnesium and ammonia (par. 100 δ. α). Or a single portion of

the acidified solution may be tested with a few drops of nitrate of barium to precipitate sulphates; then filtered and treated with excess of nitrate of silver to precipitate chlorides; then again filtered and carefully neutralized with dilute ammonia to throw down the yellow phosphate of silver which the previously free nitric acid held in solution.

The remainder of the liquid has to be evaporated to dryness, and the residue, after gentle ignition, dissolved in a small quantity of water. The solution, filtered if necessary, and acidulated with hydrochloric acid, is carefully evaporated down in a watch-glass or capsule, when cubes of common salt will crystallize out, showing the presence of **sodium.** The mother liquor from these crystals is then to be treated with perchloride of platinum and alcohol, when, on stirring, a crystalline yellow precipitate of platino-chloride of **potassium** will be deposited. Or the solution, acidified with hydrochloric acid, may be treated at once with perchloride of platinum and alcohol, the yellow liquid filtered from the potassium precipitate and evaporated down, when yellow crystals of platino-chloride of sodium will make their appearance.

§ II.—NORMAL URINE.

(155.) General Properties.

a. **Appearance, &c.** Healthy human urine is an aqueous liquid in which various compounds, organic and mineral, are dissolved, and certain other substances held in suspension. It has an amber color, a slightly acid reaction, a characteristic though not powerful odor, and a sp. gr. usually ranging within a few degrees of 1020. The substances suspended in urine are epithelium and mucus. Its dissolved organic constituents are urea, uric acid, and hippuric acid, with coloring and other extractive matters. Its

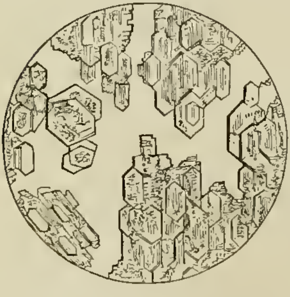
inorganic or mineral constituents are sodium, potassium, calcium, and magnesium, in the form of phosphates, sulphates, and chlorides. The student is expected to identify these several substances, to make himself acquainted with their characteristic appearances, and to realize their principal reactions. A good quarter-inch object-glass is requisite for microscopic examination.

β. **Mucus, epithelium, &c.** Recent urine set aside for some little time in a glass vessel gradually deposits a loose flocculent sediment, readily visible upon holding the specimen between the eye and the light. When examined microscopically it is seen to consist of epithelial cells, derived from different portions of the urinary apparatus, together with granular or mucus-corpuscles. By filtration, these suspended urinary constituents remain on the filtering paper as a scarcely visible deposit, while the urine itself passes through perfectly bright. On gently drying the filtering paper, the deposit assumes a varnish-like aspect.

(156.) Urea.

α. **Its detection.** A little of the filtered urine, concentrated by careful evaporation in a watch-glass, and treated with a few drops of strong colorless nitric acid, yields either at once or very speedily a crystalline deposit of nitrate of urea. This deposit, when examined under the microscope, is seen to consist of delicate six-sided plates, superimposed upon one another so as usually to prevent more than three or four of the sides of any one crystal being recognizable, as shown

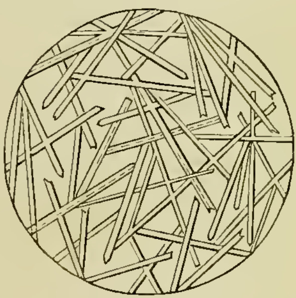
Fig. 53.



in Fig. 53. The nitrate of urea may be formed in a watch-glass and then transferred to a slide, or it may be dissolved in water and recrystallized on a slide, or nitric acid may be added to some concentrated urine previously placed in the field of the microscope, and the actual process of crystallization observed.

β. **Preparation of urea.** A couple of ounces or so of fresh and filtered urine are evaporated on a water-bath or gently heated sand-bath to a syrupy consistency, and a quantity of strong colorless nitric acid about equal in bulk to the concentrated urine added thereto, when the mixture, upon cooling, becomes semi-solid from the formation of nitrate of urea. The crystalline mass is drained on a tile, or pressed between several folds of blotting-paper, then dissolved in a little warm water, and the resulting solution treated with an excess of carbonate of barium. Upon concentrating the filtered liquid, nitrate of barium crystallizes out first, while urea remains in the mother liquor, which is evaporated to dryness over a water-bath. From this residue warm alcohol extracts the urea, and on cooling or slow evaporation, deposits it in the form of long flattened prismatic crystal, as shown in Fig. 54.

Fig. 54.



γ. **Properties of urea.** Urea behaves in some respects like an organic base, being capable of uniting with certain acids, notably the nitric and oxalic acids, to form salts. It dissolves readily in water and alcohol, producing solutions which are neutral to test-paper. The formula of urea is CH_4N_2O, and that of nitrate of urea $CH_4N_2O.HNO_3$. Urea is isomeric with cyanate of ammonium NH_4CNO, which undergoes spontaneous conversion into it; and

also isomeric, if not identical, with carbamide $N_2H_4(CO)''$. Heated with water under pressure, it is transformed into carbonate of ammonium, thus: $CH_4N_2O + 2H_2O = (NH_4)_2CO_3$. The same change takes place spontaneously in putrefying urine, and is also brought about by acting on urea with strong potash or sulphuric acid, except that the resulting carbonate of ammonium is then broken up by the reagent employed. 1000 parts of urine contain, on the average, about 15 of urea.

(157.) Uric Acid.

α. **Its detection.** This compound occurs but in small quantity in healthy human urine, 100 parts of which contain, on the average, not more than half a part of uric acid. In order to detect its presence, a couple of ounces or so of filtered urine are reduced to one-half the original bulk by evaporation, a little hydrochloric acid added to the concentrated liquid, and the whole set aside in a cool place for some hours, when the interior of the vessel will be found studded with small brown crystals of impure uric acid. In the case of urine having a moderately high specific gravity, concentration is unnecessary. After pouring off the supernatant liquid, the crystals are detached, washed with water, and dissolved in a few drops of warm potash. The resulting solution of urate of potassium is then filtered, and acidulated with hydrochloric acid, whereby a crystalline precipitate of uric acid is thrown down, which may be examined microscopically and by the action of nitric acid, as described below.

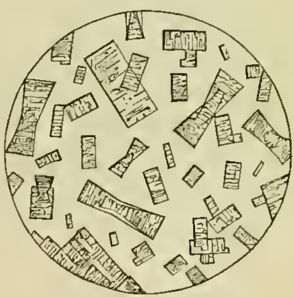
β. **Preparation of uric acid.** Uric acid cannot well be prepared, in any quantity, from normal human urine. But it may be easily obtained from the common brickdust urinary deposit, collected on a filter and washed with water; or from powdered uric calculi; or the excreta of serpents. Any one of these substances is boiled with caustic potash, the so-

lution diluted with water, filtered, and supersaturated with hydrochloric acid, whereby a very considerable opacity is at first produced, which, however, speedily disappears, and is replaced by a dense crystalline precipitate, from which the supernatant liquid may be readily poured off.

γ. **Properties of uric acid.** Uric acid furnishes two classes of salts, acid and neutral, and is consequently dibasic. Its formula is $C_5H_4N_4O_3$. The formula for a scarcely soluble or acid urate is $C_5MH_3N_4O_2$, and that for a soluble or neutral urate $C_5M_2H_2N_4O_3$. Uric acid itself is extremely insoluble, both in water and alcohol; but is soluble in alkaline solutions, forming neutral urates, and reprecipitated therefrom on the addition of an acid. It always occurs in the crystalline state, the appearance of the crystals, however, being very various. Occasionally the acid is met with in its normal form of the rhombic prism, more frequently in rhombic plates with the obtuse angles more or less rounded off, or in acuminated doubly-convex lozenge-shaped plates, or in elongated flat plates with excavated ends. Some of the forms of uric acid crystals are shown in Figures 55 and 56.

Fig. 55.

Fig. 56.



Uric acid dissolves readily, with effervescence, in nitric acid, and on evaporating the solution to dry-

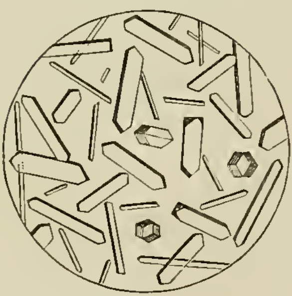
ness an amorphous pinkish residue is left. This, when moistened with ammonia, assumes a fine crimson color, which is changed to violet on the addition of a small quantity of caustic potash.

(158.) HIPPURIC ACID.

α. **Its Preparation.** Although this acid exists, in healthy human urine, in nearly the same proportion as uric acid, yet its presence therein does not so readily admit of demonstration. It can, however, be easily procured from the urine of herbivora, and from that of patients who have been taking benzoic acid as a medicine. To prepare it from either of these sources the recent filtered urine is evaporated down to one-fourth of its bulk, and then treated with an equal volume of ordinary hydrochloric acid, when, on cooling, long prismatic needles of impure hippuric acid crystallize out. These, after being washed with a little cold water, are dissolved in boiling water, and the solution set aside to crystallize.

β. **Properties of hippuric acid.** The hippuric is a monobasic acid, represented by the formula $C_9H_9NO_3$. It is soluble in water, alcohol, and ether. The crystals obtained by cooling the hot aqueous solution on a slide consist of delicate prisms, often presenting the appearance of elongated six-sided plates, as shown in Fig. 57.

Fig. 57.



By prolonged boiling with concentrated hydrochloric acid, hippuric or glyco-benzoic acid absorbs a molecule of water, and breaks up into benzoic acid and glycocine or sugar of gelatine, thus: $C_9H_9NO_3 + H_2O = C_7H_6O_2 + C_2H_5NO_2$. The larger proportion of the former product is dissipated by evaporation;

but the glycocine may be detected by adding to the liquid a drop or so of aqueous sulphate of copper and an excess of potash, whereby a deep blue-colored solution is produced, unaffected by ebullition.

(159.) Coloring and Extractive Matters.

α. **Purpurine, &c.** When healthy urine is boiled in a test-tube with about one-fourth its bulk of hydrochloric acid, a deep brownish-purple color is produced, due to the metamorphosis of a peculiar highly carbonized pink coloring matter, known as purpurine. The common pink deposits of alkaline urates owe their color to this purpurine, which has a great tendency to become precipitated with them. Hence, when perfectly white urate of ammonia, boa's excrement, for instance, is boiled in urine containing much purpurine, it is deposited on cooling of a pink color, from its carrying down some purpurine with it. When these colored deposits, natural or artificial, are boiled in alcohol, the purpurine is dissolved, forming a pinkish-red solution. The relation in which purpurine stands to the yellow coloring matter of urine is not satisfactorily established.

β. **Extractives.** The remaining organic urinary constituents are called by this name. They generally amount to about one per cent. of the urine. Included among them is some principle containing sulphur in an unoxidized form, also kreatine and kreatinine, substances derived from the oxidization of muscle, and found more largely in the juice of flesh. Schunck has noticed in urine the habital presence of a substance, allied to indican, decomposable by an absorption of water into grape sugar and indigo-blue.

(160.) Mineral Salts.

α. **Ash of urine.** This may be examined according to the directions previously given for the analysis of animal ashes (par. 144). It will be usually found

to contain calcium, magnesium, sodium, and a small quantity of potassium, in the form of carbonates, sulphates, phosphates, and chlorides. The residue left after the ash has been acted upon by acid, consists principally of carbon. When this residue is ignited for some time, a minute white ash remains, which is said to contain silica and fluorine.

β. Most of the inorganic constituents of urine may be detected in the secretion itself after simple filtration. On the addition of ammonia a white precipitate is produced, which, when examined microscopically, is seen to consist of amorphous granules of **phosphate of calcium** and characteristic stellate feathery crystals of **ammonio-phosphate of magnesium.** If healthy urine, especially that passed after a night's rest, be evaporated very gradually upon a glass slide, minute octahedral crystals of **chloride of sodium** may be detected by microscopic examination. Generally speaking, however, the common salt is seen in the form of very complex right-angled crosslets (stauroid crystals), arranged somewhat like *chevaux de frise.* On the axes and extremities of these forms, octahedrons may occasionally be recognized by a good defining glass. Fig. 58 shows one of the many appearances presented by carefully evaporated urine.

Fig. 58.

Sulphuric and hydrochloric acids may be detected in urine by the usual tests.

§ III.—ABNORMAL URINE.

The abnormal constituents of urine which do not necessarily give rise to deposits, are albumen, sugar, biliary matters, and fat.

(161.) Albuminous Urine.

α. **Appearance, &c.** The general appearances of albuminous urine vary considerably. Sometimes it presents nothing unusual in its aspect; often the flocculent deposit formed by repose is larger in amount than that of the healthy secretion; occasionally the urine has a faintly opalescent appearance, not removable by filtration; and very frequently it is met with, black, brown, or red, from the presence of altered blood, with or without the occurrence of a deposit of blood globules. Albuminous urine when shaken retains the froth for a long time; its specific gravity is very variable.

β. **Test by boiling.** Some of the suspected urine is boiled in a test tube, when, should albumen be present, a turbidity will be produced, the amount of which may vary from a faint cloud to a bulky precipitate rendering the urine nearly solid. *Impediments.*—*a.* Albumen when dissolved in alkaline fluids is not necessarily deposited upon boiling, the formation or non-formation of a precipitate having reference to the relative quantities of albumen and alkali respectively present. Therefore, in testing an alkaline urine for albumen, the liquid should first be rendered *very faintly* acid with acetic acid. *b.* A previously opaque condition of the urine interferes with the action of this test. This interference may be lessened, if not removed, by filtering the urine before applying heat thereto. In urine containing deposits, the clear liquid can generally be poured off and tested separately. But deposits of urates do not impede the action of this test, as, upon heating the urine, their dissolution takes place before the precipitation of any albumen. *c.* Albuminous urine, to which a very minute quantity of nitric acid has been added, is not rendered turbid by heat. *Fallacy.*—Upon boiling certain varieties of urine, a precipitate of the earthy phosphates occasionally takes place,

which can, however, be distinguished from that of albumen by the addition of a little dilute nitric acid, whereby the former is dissolved, the latter unaffected.

γ. **Nitric acid test.** On adding nitric acid to albuminous urine, a white turbidity is produced, varying in amount with the proportion of albumen present. *Impediments.—a.* The reagent should be added drop by drop, since a minute quantity does not cause any precipitate, and a great excess dissolves any precipitate which may have formed. *b.* When the urine is opaque, it should be rendered slightly alkaline with potash, agitated, filtered, and then tested with nitric acid. *Fallacies.—a.* In some varieties of urine the addition of nitric acid produces a precipitate of uric acid, which, however, speedily shrinks very much in bulk, and, when examined microscopically, is seen to be crystalline, whereas the deposit of albumen is amorphous. *b.* Nitric acid produces a whitish turbidity in the urine of patients who have been taking copaiva, cubebs, and probably other oleo- and resinous medicines. But while the precipitate of albumen subsides to the bottom of the test-tube in the course of a few hours, the precipitate of oleo-resinous matters remains suspended in the urine for two or three days. Moreover, inquiry can always be made on these points.

δ. **Ferrocyanide of potassium test.** Solution of ferrocyanide of potassium added to albuminous urine previously acidulated with acetic acid, throws down a white precipitate. *Impediment.*—The mere addition of acetic acid to urine occasionally produces a precipitation of mucus, in which case the acidulated urine must be filtered before being tested with ferrocyanide.

(162.) Saccharine Urine.

α. **Appearance, &c.** Saccharine urine cannot be distinguished by the eye from the normal secretion. It has generally a high specific gravity, a rather

fragrant odor, and when agitated retains its froth for some time. It is said to have a distinctly sweet taste. Minute traces of sugar exist habitually in normal urine.

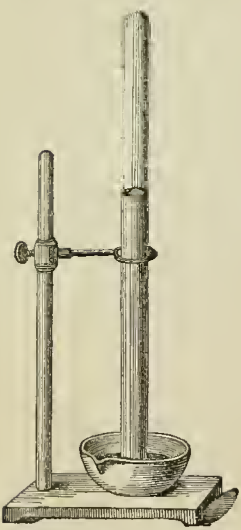
β. **Potash test.** To the suspected urine, an equal bulk of the ordinary solution of caustic potash is added, and the whole boiled; whereon a deep orange-brown, frequently almost black, color is produced if sugar be present in abnormal quantity. *Fallacies.*—Should a deep brown color be produced, the test is free from fallacy; but there are many specimens of non-saccharine urine which, when boiled with caustic potash, acquire a tolerable dark sherry color. Moreover, caustic potash frequently contains lead, and this impure reagent, acting upon the sulphur of ordinary urine, or more decidedly in albuminous specimens, will occasion a brown discoloration. The potash should, therefore, be first tested for lead.

γ. **Copper test.** The urine is mixed with about its bulk of caustic potash solution, whereby a precipitate of earthy phosphates is produced, which, in questionable cases, should be separated by filtration. To the alkaline liquid, filtered or unfiltered, a drop or two of a dilute solution of sulphate of copper is added, when, if sugar be present, the greenish-blue precipitate first thrown down will disappear upon agitation, forming a deep blue-colored liquid. On heating this liquid, and even before it arrives at the boiling point, a red or orange-colored precipitate will be formed, characteristic of sugar. *Fallacies.*—Although the precipitate produced by the addition of sulphate of copper to a mixture of normal urine and caustic potash does not disappear upon agitation, still the disappearance of the precipitate with formation of a blue liquid is no proof of the presence of sugar. Moreover, the application of heat should not be continued after the blue liquid has acquired a boiling temperature, as many substances by prolonged ebullition effect a deposition of the red suboxide of copper.

δ. **Modified copper test.** Instead of taking separate solutions of sulphate of copper and potash, a ready-made alkaline solution of tartrate of copper may be added to the suspected urine, and the whole heated to the boiling point, when the production of an orange precipitate of suboxide of copper will show the presence of sugar. The test solution is made by dissolving about 20 grains of sulphate of copper and 40 grains of neutral tartrate of potassium in an ounce of the officinal solution of potash, whereby a clear deep blue liquid should be produced, which may be filtered if necessary.

ε. **Tin test.** The reduction of salts to tin, bismuth, silver, and chromic acid by grape sugar at a moderate heat, have been made the bases of separate tests. The tin test is best performed by having ready-prepared strips of merino or other woollen (not cotton or linen) tissue dipped in solution of dichloride of tin and then dried in a water-bath. On moistening one of these strips with diabetic urine, and holding it near the fire, or otherwise heating it to a temperature of about 300° F., a brownish-black coloration quickly makes its appearance. This is a convenient clinical test, and one of great delicacy.

Fig. 59.



ζ. **Fermentation test.** Ordinary yeast, or the dried German yeast, is mixed with water, and a long test-tube completely filled with the suspected urine, to which a little of the yeast liquid has been added. The tube is then closed with the thumb, and inverted in a saucer containing a little of the urine

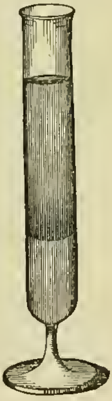
under examination, so that no air may enter the tube; and the whole set aside in a tolerably cool situation. The temperature ought not to be below 70° Fahrenheit. Should the urine be saccharine, minute air-bubbles will speedily make their appearance, and in the course of an hour or so a very definite quantity of gas will occupy the upper part of the tube, as shown in Fig. 59; but other forms of apparatus may be employed. The sporules and thallus of the sugar fungus, or yeast plant, are said to be recognizable in stale saccharine urine.

(163.) Biliary Urine.

α. **Appearance, &c.** Biliary urine has a yellowish-brown color, and a persistent bitter taste. It is doubtful whether the urine as voided ever contains more than a trace of the true biliary salts, for the detection of which substances only is Pettenkofer's test adapted (*vide* par. 178); but Heller's test, and the nitric aid test, react upon the coloring matter of bile, which not unfrequently finds its way into the urine.

β. **Nitric acid test.** A little of the urine, previously concentrated if necessary, is poured on to a white plate, so as to form a thin layer, upon which a few drops of strong nitric acid are then let fall. Where the acid comes into contact with the biliary urine, a peculiar play of colors is produced—green, pink, violet, and yellow, being readily recognizable. Or a mixture of the urine with dilute nitric acid may be carefully poured on to some strong sulphuric acid, when the characteristic coloration will take place at the junction of the two liquids, as seen in Fig. 60.

Fig. 60.



γ. **Heller's test.** For the application of this test the urine is required to

contain albumen; hence it must be mixed, if necessary, with a little diluted white of egg, serum of blood, or some other urine containing albumen. Nitric acid is then added, when, if bile be present, the precipitate will have a faintly bluish or greenish color; but the test is not very satisfactory.

(164.) Fatty Urine.

α. **Fat globules, &c.** The conditions in which fat occurs in the urine have not been ascertained with any degree of precision. Occasionally, when examining the ordinary flocculent deposit of urine by means of the microscope, isolated fat globules may be recognized. Fat occurring only in this state is believed by some observers to be necessarily of extraneous origin. In some forms of Bright's disease the fibrinous casts of tubes and the epithelial cells, particularly those derived from the kidney, are seen loaded with fat, and at the same time isolated fat globules may be detected.

β. **Chylous urine.** Occasionally this curious variety of urine is met with: the secretion is more or less opaque, always contains albumen, frequently gelatinizes on cooling, and, when, examined microscopically, displays an abundance of minutely divided granular matter, and a few granular cells similar to those found in the chyle, but no fat globules. Fat, however, may be readily obtained by agitating the urine with ether, and evaporating the ethereal solution.

γ. **Kiestein-urine.** In the urine of pregnant women the so-called kiestein may be recognized. The secretion has generally an acid reaction, and by repose becomes faintly opaque. In the course of two or three days a fat-like scum rises to the surface, remains there for two or three days, and then sinks to the bottom of the vessel, the urine becoming at the same time ammoniacal. When this scum is examined microscopically, it is seen to consist of crystals of

triple phosphate, with a few fat globules, imbedded in a dense granular matter, which appears to be of an albuminous character, containing, however, minutely divided fat. Kiestein urine, by keeping, frequently evolves a powerful odor of putrescent cheese. Its occurrence is no longer regarded as positively diagnostic of pregnancy.

§ IV.—URINARY DEPOSITS.

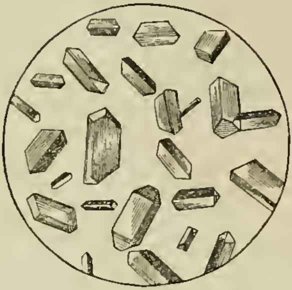
These may be distinguished into chemical compounds either crystalline or amorphous, and structural or organized compounds.

(165.) Chemical Deposits.

α. **Urates or lithates.** *Every deposit which disappears upon the application of heat, consists of uric acid in combination with various bases.* These urates are sometimes white, but generally more or less colored with purpurine, which may be partially extracted from them by means of boiling alcohol. They form a bulky deposit, nearly always amorphous, occasionally appearing in the form of minute spheres with protruding spicula. Urate sediments dissolve readily on the addition of caustic potash, the solution when boiled giving off ammonia. Moreover, they yield a residue of murexide, when treated with strong nitric acid, evaporated to dryness, and held over the vapor of ammonia. The urine in which these deposits occur has generally an acid reaction.

β. **Earthy phosphates.**—*Nearly every deposit which disappears upon the addition of hydrochloric acid consists of earthy phosphates.* These salts form a bulky opaque white deposit, which, unless associated with mucus, is easily diffusible upon agitation. The urine itself is mostly alkaline, or neutral, or but very faintly acid. Deposited phosphate of calcium is usually amor-

Fig. 61.



phous, save in acid urine, where it sometimes occurs in peculiar radiated or penniform crystals. The ammonio - phosphate of magnesium crystallizes in variously modified triangular prisms, often simulating irregular six-sided plates, as shown in Fig. 61; and in very ammoniacal urine is met with in the form of stellate feathery crystals. In some cases this deposit is seen as an iridescent pellicle, and occasionally it remains for a long time suspended in the urine.

γ. **Uric acid.**—*Every obviously crystalline deposit, having a distinctly yellow or red color, consists of uric acid.* The color, specific gravity, and acidity of urine yielding uric acid sediments are generally rather above than below the average. The deposit is compact in its appearance, and subsides quickly after agitation. It is readily soluble in potash, from which solution it is reprecipitated on the addition of hydrochloric acid. When treated with strong nitric acid, evaporated to dryness, and held over the vapor of ammonia, it yields murexide. Uric acid deposits are very rarely indeed devoid of color. They are met with in variously modified crystalline forms (*vide* par. 147).

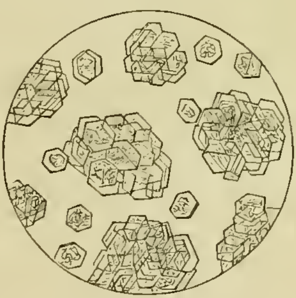
δ. **Oxalate of calcium.** This salt seldom if ever forms a distinct sediment. It may be detected by allowing the urine to stand at rest for some time, and then pouring away all but the last portions, which must be examined microscopically. It occurs in well-marked octahedrons, the crystals generally appearing to have a square outline, and their opposite angles being connected by markings, as shown in Fig. 62.

Fig. 62.

The sediment may be rendered apparent to the naked eye, by warming the residue of urine, left after pouring away the greater portion, giving it a rotatory motion, and allowing it to stand for a few minutes. Then on pouring off the remainder of the urine, and replacing it by water, a white glistening deposit becomes visible. The deposit of oxalate of calcium is scarcely at all affected by cold potash. It dissolves without effervescence in dilute hydrochloric acid, forming a solution which effervesces on the addition of a little peroxide of manganese. There are occasionally found associated with octahedrons of oxalate of calcium, certain dumb-bell-shaped crystals, said to consist of oxalurate of calcium. They are insoluble in potash, soluble in hot hydrochloric acid, and when incinerated leave a residue of carbonate of calcium. Deposits of uric acid and phosphates have been occasionally met with in the dumb-bell form.

ε. **Cystine.** This deposit occurs somewhat rarely, in the form of a bulky, easily diffusible deposit, resembling in its appearance the white or pale lithates. When examined microscopically it is seen to consist of rosette-like plate, in which a hexagonal outline may sometimes be recognized. After pouring off the supernatant urine, the sediment will be found to be insoluble in acetic acid, soluble in hydrochloric acid, and very soluble in

Fig. 63.



ammonia. When the ammoniacal solution is allowed to evaporate spontaneously on a slide, very well-defined, transparent hexagonal plates crystallize out, as shown in Fig. 63. Cystine is remarkable for containing twenty-six per cent. of sulphur, so that when cystic urine is boiled with a solution of acetate of lead to which potash has been added in sufficient excess to dissolve the precipitate at first thrown down, the whole becomes nearly black, from the formation of sulphide of lead. Cystic urine has when recent an aromatic, when decomposing a very fetid odor. The formula of cystine is $C_3H_7NSO_2$.

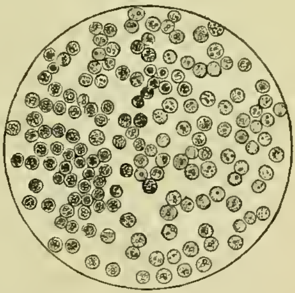
(166.) Organized Deposits.

α. **Normal sediment.** A flocculent deposit, varying slightly in quantity and appearance, always separates from urine by repose. When examined microscopically it may show, in addition to the usual mucus-corpuscles and epithelium-cells, torulæ characteristic of saccharine urine, casts of uriniferous tubes indicative of Bright's disease, fat globules, whether free or contained in a cell wall, vibriones, spermatozoa, blood globules, exudation globules, minute crystals of oxalate of calcium, and occasionally of uric acid, &c. &c.

β. **Pus.** This substance presents a different appearance accordingly as it occurs in acid or alkaline urine. In acid urine, purulent deposits sink to the bottom of the vessel, and form a greenish-yellow opaque layer, having a creamy consistency, an easy diffusibility on agitation, and a slow subsidency on repose, gelatinizing when agitated with an equal bulk of caustic potash, and in fact presenting all the ordinary qualities, physical and microscopical, of pus. In alkaline urine the deposit is viscid, tenacious, ropy, not diffusible on agitation, and is mixed up with the earthy phosphates, which may, however, be separated by the action of dilute hydrochloric acid. Purulent urine is necessarily albuminous. When a

deposit of pus has been agitated with ether, the resulting ethereal solution, upon being poured off and evaporated, leaves a considerable residue of oily globules.

Fig. 64.



The pus corpuscles, which, however, can scarcely be said to exist after the action of an alkali, consist of circular granulated cells, somewhat larger than blood globules, as shown in Fig. 64. When acted on by acetic acid, they swell up very considerably, their margins become distinct, and two, three, or four small granular masses appear in their centres.

γ. **Mucus.** A little mucus is always met with, even in normal urine. It may be much increased in quantity without being appreciably altered in character; but oftener it occurs in the form of gelatinous masses, which sink to the bottom of the vessel, or, from the entanglement of air-bubbles, remain for a long time suspended in the urine.

Mucus deposits have a more or less marked alkaline reaction, even when the supernatant urine is acid: they do not diffuse readily by agitation, and are frequently associated with a very considerable sediment of the earthy phosphates. The presence of even a large amount of mucus does not of itself render the urine albuminous. The microscopical characters of the mucus corpuscle are very similar to those of the pus corpuscle, but the granular character is perhaps not quite so well marked.

δ. **Blood.** Urine containing blood is necessarily albuminous. On allowing the urine to stand, and examining the sediment microscopically, blood globules may be recognized by their uniform size, non-

granular surface, and yellow color. The appearance of urine containing blood is very variable; its color may be light-red, dark-red, reddish-brown, smoke-brown, or scarcely altered. The sediment also varies much in its appearance; sometimes its nature is evident to the unassisted eye, at other times it occurs but in very minute quantities, and can only be identified microscopically. Urine may contain altered coloring matter of blood, and yet the blood-corpuscles escape recognition.

§ V.—CLINICAL EXAMINATION OF URINE.

(167.) General Examination.

α. **Appearance, &c.** It is advisable to notice the color, whether pale from a dilute urine, or dark from a concentrated urine, or reddish-yellow from purpurine, or brownish-yellow from bile, or red or brown from blood—the taste, whether sweet from sugar, or bitter from bile—the smell, whether fragrant from cystine or from sugar, or fetid from alkalinity, with or without mucus, or from cystine—any opalescence or milkiness due to fat, kiestein, mucus, or a modification of albumen, &c.

β. **Specific gravity.** The specific gravity should be taken by means of a gravimeter (Fig. 65). It may be too low, from an accidentally diluted urine, or from *Diabetes insipidus*, or from certain forms of *Morbus Brightii*, &c.; too high, from a concentrated urine or from the presence of sugar, &c. Dr. Golding Bird pointed out the very curious coincidence, that the last two figures, expressing the specific gravity, represent very nearly the number of grains of solid matter contained in an ounce of the secretion; thus in urine of the specific gravity 1017, every fluidounce contains about 17 grains of solid matter. This, however, must be regarded as but a very rough approximation to the

truth, trifling variations in the amount of the saline constituents of urine effecting greater alterations of density than considerable variations in its organic constituents.

Fig. 65.

γ. **Quantity.** In order to determine the quantity of urine passed in twenty-four hours, the patient should be caused to make water at some definite hour in the day, say 10 A. M., the amount then voided being neglected. After this he should save all the urine he passes until 10 o'clock on the next day, at which time he must again empty his bladder, and add the contents to the specimen to be measured. He should moreover be desired always to micturate before going to the closet. By multiplying the number of ounces passed, by the last two figures of the specific gravity, an approximation will be arrived at as to the total amount of solids excreted by the kidneys in twenty-four hours.

(168.) Chemical Examination.

α. **Reaction to test-paper.** Normal urine has a slightly acid reaction. If alkaline, it will restore the blue color of reddened litmus-paper. Should the blue color remain after the paper has become dry, the alkalinity is due to the presence of a fixed alkaline salt; but should the red color reappear on drying the paper, the alkalinity is due to ammonia.

β. **Testing the urine.** The supernatant urine is to be poured away from any deposit which may have formed, and be examined for albumen, sugar, purpurine, and if necessary fat and bile. Should the

urine have a high specific gravity and be free from sugar, it may be examined for an excess of urea by pouring a little of the secretion into a watch-glass, and adding about two-thirds its bulk of cold concentrated nitric acid. The formation of a crystalline deposit of nitrate of urea is, with certain restrictions, indicative of an excess of that base. It is, perhaps, generally advisable to concentrate the urine slightly before adding the acid.

γ. **Testing the deposit.** The appearance of the deposit generally indicates the order in which the tests, both microscopical and chemical, should be applied. The lithates are dissolved by heat, dissolved by potash, undissolved by hydrochloric acid; the phosphates are undissolved by heat, undissolved by potash, dissolved by hydrochloric acid; uric acid is undissolved by heat, dissolved by potash, undissolved by hydrochloric acid; cystine is undissolved by heat, dissolved by ammonia or potash, and dissolved by hydrochloric acid; oxalate of calcium is undissolved by heat, undissolved by potash, dissolved by hydrochloric acid. In mixed deposits the different ingredients are readily recognized by their different microscopical appearances, and by their different behavior with the above reagents.

§ VI.—URINARY CALCULI.

(169.) General Characters.

α. **Construction, &c.** Urinary calculi are for the most part built up of concentric layers. This structural arrangement is readily seen on making a section of a calculus through its centre. All the layers of a calculus may have the same composition, or may differ very much from one another in this respect. One single uniform layer of a calculus may be, and generally is, composed of several ingredients.

Fig. 66.

The internal arrangement of a mixed mulberry and fusible calculus, belonging to the museum of St. Bartholomew's Hospital, is shown in Fig. 66 (No. 79 in catalogue).

It is probable, that if a very exact analysis were made, each of the layers of nearly every calculus would be found to contain uric acid, alkaline urates, phosphate of calcium, and ammonio-phosphate of magnesium, with or without the other constituents of calculi. Moreover, most calculi contain traces of all the salts naturally existing in the urine, as well as of coloring matter, mucus, &c.

From these considerations it is obvious that the chemical examination of a calculus need have reference only to its general composition, and not to its exact analysis. It is important, however, to bear in mind, that even a homogeneous layer of a calculus rarely ever consists of one constituent only.

β. **Appearance, &c.** The general appearances, &c., of the different varieties of calculi are as follows: *a.* **Uric calculi** consist of uric acid, with or without variable proportions of the alkaline urates. They have usually a uniform outline, a compact laminated structure, and an orange or yellow color: sometimes the laminated appearance is wanting, and sometimes they have a light fawn color, resembling the paler varieties of oxalate of lime concretions. A greater or less amount of uric acid is found in the centres of most calculi.

b. **Earthy phosphates** consist of phosphates of calcium and ammonio-phosphate of magnesium. It rarely if ever happens that where one of these constituents is present the other is wholly absent. When

the two exist in about equal quantities, the concretion is known by the name of the *fusible calculus*, in consequence of the readiness with which it fuses in the blowpipe flame. But when either constituent is present in great excess, this fusion cannot be effected. The distinctly laminated character appears to be more frequently wanting in the fusible than in most other varieties of calculi. Phosphatic calculi differ much in their appearance; they have usually a smooth uniform surface, and a pale, white, or even chalk-like aspect. Sometimes they are compact and hard, at other times light ahd friable; sometimes the layers adhere very closely to one another, and at other times are just as easily separable. The earthy phosphates may constitute the greater part of a calculus, or may be disseminated through the other constituents, or may form distinct layers: they give a more or less thick external coating to most calculi.

c. **Oxalate of calcium** calculi are generally recognized by their dark color, hard, compact, laminated structure, and irregular surface. The term mulberry calculus does not give any idea of the degree of this irregularity. But some small oxalate of calcium calculi, known as hemp-seed concretions, have a smooth contour. Occasionally, oxalate of calcium concretions, especially when forming layers in other calculi, or when mixed with uric or phosphatic deposits, have a pale color, and very finely laminated structure. The central portions of oxalate of calcium calculi generally contain more or less uric acid.

d. **Cystine** calculi are of comparatively rare occurrence. They have an irregular or oval shape, a rough and crystalline-looking surface, a fawn-brown color when recent, and a sea-green color when long kept. Cystine rarely ever enters into the constitution of composite calculi.

γ. **Action of heat.** Some of the ingredients of calculi are destructible by heat, some indestructible, as seen in the following table:—

Destructible.

- Uric Acid.
- Urate of Ammonium.
- Cystine.
- Oxalic Acid, from oxalate of calcium.
- Ammonia, from triple phosphate.
- Uric Acid, from urates of calcium and sodium.

Indestructible.

- Phosphate of Calcium.
- Carbonate of Calcium.
- Phosphate of Magnesium, from triple phosphate.
- Carbonate of Sodium, from urate of sodium.
- Carbonate of Calcium, from oxalate and urate of calcium.

If the heat be sufficiently prolonged and intense, the carbonate of calcium will become converted into caustic lime. Carbonate of calcium is not an unfrequent constituent of calculi which have undergone partial decomposition in the bladder.

(170.) Preliminary Examination.

a. **Pulverization, &c.** The calculus to be examined should be sawn through its centre, so as to expose its internal arrangement. Should it consist of layers obviously differing from one another, each of them must be separately examined. For this purpose, a sufficient quantity of each layer may be consecutively removed by means of a pocket-knife. The determination of the nature of any one layer should be ascertained before removing a specimen of the next one. In friable calculi, great care must be exercised in obtaining specimens of the different layers. The smooth appearance of the flat surface can be readily restored by grinding, so that a calculus may be analyzed without any necessary disfigurement. The specimen removed from each layer is to be reduced to a fine powder.

β. **Ignition.** A little of the powder is to be heated upon platinum foil, and careful attention paid to any of the following results, &c.

Charring. All urinary calculi undergo a slight amount of charring. In oxalate of calcium calculi this is very slight, and speedily disappears, leaving a bulky white pulverulent residue. In phosphatic calculi the charring is more complete, and the carbon not so easily burnt off.

Decrepitation. This is always very slight; when occurring simultaneously with the formation of a white smoke and a great degree of mobility in the heated powder, it is indicative of urate of ammonium.

Odor. Oxalate of calcium calculi do not evolve much odor when heated; most others do. The odor produced by the ignition of cystine is well marked and characteristic.

Volatilization. Should the calculus powder burn away almost entirely, it will suffice to test for uric acid, urate of ammonium, and cystine.

Fusion. The heat of a spirit-lamp is sometimes sufficient to fuse the mixed earthy phosphates.

Alkalinity. When only the heat of a lamp has been employed, any alkalinity to test paper, shown by the moistened residue, is probably due to carbonate of sodium, derived from the ignition of urate of sodium.

Effervescence. The moistened residue is treated with a drop or two of nitric acid. Effervescence denotes the presence of a carbonate, whether originally existing as such, or derived from the ignition of oxalate of calcium or of the fixed alkaline urates; in which latter case the amount of effervescence is usually very small.

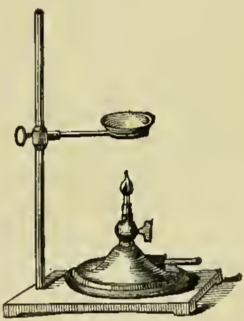
Blowpipe. Should the ordinary flame have proved incapable of fusing the ash, the acidified residue may now be dried, and strongly heated before the blowpipe; when, if the mixed earthy phosphates are present, a more or less complete fusion, or at any rate cohesion of the particles, will take place.

(171.) Special Tests.

In addition to noticing the above described effects of heat, it will often suffice to make special tests for the phosphoric, oxalic, and uric acids, without subjecting the calculus to a more complete analysis.

α. **Phosphoric acid.** The residue upon the foil after its ignition before the blowpipe is treated with a drop or two of nitric acid and a little water, whereby its solution is usually effected without appreciable effervescence, any carbonate of calcium having been converted into caustic lime. A drop or two of nitrate of silver solution is then added, and the mixed liquid carefully neutralized with dilute ammonia, when the production of a yellow precipitate will indicate the presence of phosphoric acid. Under certain circumstances, especially when triple phosphate constitutes the great mass of the calculus, or when the silver salt has been added in very small quantity, the precipitate is white. Or the nitric acid solution of the ignited calculus may be tested with molybdate of ammonium (vide par. 92 δ). Triple phosphate are distinguished from bone earth calculi by their solubility in acetic acid.

Fig. 67.



β. **Oxalic Acid.** Some of the original calculus powder is mixed with a drop or so of dilute sulphuric acid, and a little finely divided peroxide of manganese added, whereby any oxalic acid is at once oxidized into carbolic acid, which is liberated with effervescence.

γ. **Uric acid.** A little of the original calculus powder, placed in a watch-glass, is treated with a drop or two of strong nitric acid in which, if uric acid or a urate be present, it will dis-

solve with effervescence. On carefully evaporating to complete dryness over a small flame, as shown in Fig. 67, a pinkish residue is left, which, when cold, is to be moistened with a drop of ammonia, whereby murexide will be produced with its characteristic crimson color, convertible into violet on the addition of a little caustic potash. Or the watch-glass may be held in the fingers as a precaution against using too strong a heat.

(172.) Systematic Analysis.

α. **Solution.** Some of the powdered calculus is boiled for a few minutes with a little distilled water in a test-tube, the mixture thrown upon a filter, the filtrate collected apart, and the residue thoroughly washed with boiling water. The first portion of the washings may be reserved for use on an emergency. The filtrate *A* may contain urate of ammonium, urate of sodium, and urate of calcium.

The washed residue is next boiled in dilute hydrochloric acid, observation being made as to whether or not any effervescence indicative of the presence of carbonate of calcium takes place. The acid liquid is thrown on a filter, the resulting filtrate *B* collected apart, and the residue therefrom, if any, washed with water. The acid solution *B* may contain chloride of calcium from the decomposition of the carbonate, oxalate of calcium, cystine, phosphate of calcium, and ammonia-phosphate of magnesium. The residue *C* left upon the filter will consist of uric acid.

β. **Aqueous solution.** A few drops of the solution *A* are evaporated upon a glass plate, when, should a mere trace of residue only be left, the remainder of this solution may be disregarded, and the calculus considered as free from any appreciable amount of alkaline urates. But should an obvious residue be left, about one-fourth part of the solution may be boiled in a test tube with a little caustic potash, when **ammonia**, if present, will be given off so as to be

recognizable by its odor and by its reactions with test-paper and hydrochloric acid vapor, &c. The remainder of the solution is reduced to a very small bulk by evaporation, treated with strong nitric acid, and evaporated cautiously to dryness, when the production of a pinkish residue, rendered crimson when moistened with ammonia, will be indicative of **uric acid.** The contents of the capsule are next incinerated, the residue treated with a few drops of water, and the liquid divided into two portions. One is slightly acidified with acetic acid and tested with a drop of oxalate of ammonium, when the production of a white turbidity will indicate the presence of **calcium.** The other is acidified with hydrochloric acid and evaporated cautiously to dryness, when the production of microscopic cubical crystals will show the presence of **sodium.**

γ. **Acid solution.** By means of dilute ammonia, the solution *B* is made as nearly neutral as it can be, without having its transparency affected. Acetate of ammonia is then added, the production by which of a white precipitate will indicate the presence of **oxalate of calcium** or **cystine.** The latter body rarely occurs in mixed calculi, and could be readily separated from the oxalate by treatment with ammonia; on evaporating the ammoniacal solution, it would be deposited in the form of hexagonal tablets. To the clear liquid, if no precipitate has formed, or otherwise to the filtrate therefrom, oxalate of ammonium is added in excess, when the deposition of a white precipitate will indicate the presence of **calcium,** which did not previously exist in the state of an oxalate. Filtration is next performed, if necessary, and an excess of ammonia added to the clear liquid, when the production of a white crystalline precipitate, after stirring for a little while, will prove the presence of **phosphoric acid** and of **magnesium.** Should there be no obvious precipitate, sulphate of magnesium is to be added, when the presence of **phospho-**

ric acid will be indicated by the formation, after stirring, of a white crystalline precipitate.

δ. **Insoluble residue.** The residue *C* is to be treated with concentrated nitric acid, and the whole evaporated to dryness, whereby a pink mass will be left, which held over the vapor of ammonia will become crimson, and if subsequently moistened with potash will become purple, reactions characterizing **uric acid.**

§ VII.—BLOOD.

(173.) Coagulation.

α. Blood as existing in the vessels is seen to consist of red **corpuscles** floating in a clear liquid, termed the **liquor sanguinis.** When removed from the living vessels it speedily separates into two portions, a clear yellow liquid, the **serum**, and a solid red mass, the **clot**. The liquor sanguinis consists of fibrin and serum; the clot, of fibrin and corpuscles, as seen in the following diagram:—

$$\text{Blood.}\left\{\begin{array}{ll}\text{Liquor Sanguinis.} & \left\{\begin{array}{l}\text{Serum.}\\ \text{Fibrin.}\end{array}\right. \\ \text{Corpuscles . . .} & \end{array}\right. \quad \text{Clot.}$$

Thus the chemical investigation of the blood naturally divides itself into separate examinations of the clot and serum.

β. The coagulation of blood is due to the solidification of fibrin, which entangles in its meshes the corpuscles and a considerable portion of the serum, so as to form a firm jelly-like mass. While the blood is circulating through the vessels of living animals, the fibrin exists in a state of perfect solution. The circumstances which determine this state of solution are not well understood; but intimate contact with the living tissues appears to be one very important

condition. Out of the body the fibrin speedily solidifies, the coagulation, which is accompanied by a slight evolution of ammonia, being generally complete in about ten minutes' time. Variations of temperature, movement, and exposure to air, modify but never prevent the coagulation. Where the fibrin exists in large quantity, the coagulation takes place more slowly, but the coagulum is firmer and more compact. When blood is removed from persons suffering from an inflammatory condition of system, or when it contains an excess of fibrin, or a deficiency of corpuscles, or when it is collected in a deep narrow vessel, or when its coagulation is retarded by any means, the corpuscles sinking before the coagulation is complete, exist principally in the lower portion of the clot, while the upper layer consists of nearly colorless fibrin. This colorless layer is termed the *buffy coat;* it is extremely tenacious, and frequently by its slow contraction draws up the edges of the clot, so as to form a cup-like depression.

(174.) Fibrin.

α. **From liquid blood.** Fibrin is most easily procured from this source. The blood, before it has had time to coagulate, is rapidly whipped with a few twigs of wood, or well shaken in a bottle with two or three irregular pieces of lead. In this way the fibrin separates more or less completely from the corpuscles, and adheres to the twigs or pieces of lead in the form of loose fibrous masses. These are to be well washed with water, and also with ether, when it is desired to remove the adherent fat.

β. **From the clot.** The preparation of fibrin from coagulated blood is rather more tedious. The clot should be placed upon a cloth, thoroughly broken up by the hand, and washed under a stream of water; when, by alternate washing and kneading, the serum and coloring matter of the clot will pass through the

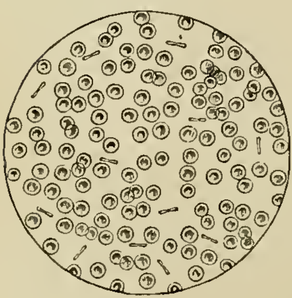
cloth, and a residue of tolerably white fibrin be left thereon.

γ. **Properties of fibrin.** Fibrin possesses all the chemical properties of coagulated albumen (*vide* par. 176 *γ*). When examined microscopically it is seen to differ from coagulated albumen in manifesting an organized structure, though of the lowest type, viz., the simply fibrous. This fibrillated arrangement is best seen in the buffy layer of inflammatory blood. When moist fibrin, especially that obtained from the clot, is covered with water rendered *faintly* alkaline by soda, and left at rest for some days in a tolerably warm situation, the greater part of it dissolves, and albumen may be detected in the filtered liquid by the action of heat and nitric acid. Fibrin constitutes about 0.25 per cent. of normal blood.

(175.) Corpuscles.

α. **Their appearance.** When a drop of uncoagulated blood, or a drop of the deep red-colored serum squeezed out of the clot, is examined under a good quarter-inch object glass with a high eye-piece, the field of the microscope is seen covered with minute colored cells, of uniform size, circular outline, and non-granular structure, as shown in Fig. 68.

Fig. 68.



According to the focussing the edges will appear dark and the centre transparent, or *vice versâ*. Some of the globules may be seen lying upon their edges, some of them adhering to one another by their flat surfaces, forming rouleaus. In the case of the previously uncoagulated blood, a delicate network of fibrin will speedily appear. Blood corpuscles

appear to consist of a transparent membrane containing a red-colored fluid. The phenomena of *osmose* may be readily seen under the microscope: thus if a concentrated solution of sulphate of sodium be added, the corpuscles become distorted, their edges uneven, and their dark centres more prominent; if, however, water be added, the corpuscles swell up, their dark centres and defined margins gradually disappear, and finally the cells burst with discharge of their contents.

In addition to the above-described red corpuscles, there may generally be seen a few of the colorless or lymph corpuscles. In healthy blood these exist in a variable but very small proportion compared with the red, than which they are rather larger in size, and less uniform in outline. Moreover, they manifest a faintly granular structure.

β. **Their separation.** If blood, as it is flowing, be received into a saturated solution of sulphate of sodium, all coagulation will be prevented, and by repose the corpuscles will form a bright scarlet layer at the bottom of the vessel. The supernatant fluid may be poured off, and the sediment collected in a filter, and washed with a solution of sulphate of sodium. Or the red liquor, from which the fibrin has been removed by agitation, may be allowed to subside; or the clot may be broken up, well shaken with the serum, and the red fluid so formed be allowed to subside. From either of these fluids a gradual but incomplete deposition of the corpuscles will take place. The supernatant serum may then be poured away, and replaced by a solution of sulphate of sodium, when the corpuscles will behave as in the first instance, and may be collected upon a filter and washed with sulphate of sodium as before.

γ. **Red coloring matter.** Hæmatosine, or the red coloring matter of blood, is remarkable for the amount of iron which it contains. The ash of blood corpuscles yields fully 30 per cent. of peroxide of

iron. The presence of iron in any of the other tissues or fluids, with the exception of the chyle, appears to be due to an admixture of blood. It is possible indeed to obtain a modified hæmatosine free from iron; but no inference can be drawn from the experiment. The chemical reactions of the coloring matter may be recognized by throwing the corpuscles, well washed with sulphate of sodium and drained, into a considerable excess of cold water, when the cell walls burst by endosmosis, and the colored contents of the cells dissolve in the water, forming a deep-red solution, which by filtration may be made perfectly bright. This red coloring matter is unaffected by ammonia, and is entirely destroyed by ebullition, with the formation of a dirty-colored coagulum, which dissolves in caustic potash with an indistinct greenish color.

δ. **Hæmatocrystallin,** or **blood crystals.** The formation of these crystals was first discovered by Dr. Otto Funke, of Leipsic. It appears that by the bursting of the red corpuscles as above described an aqueous solution of their contents is obtained, which by very slow evaporation yields crystals having very definite forms. The blood of some of the lower animals, particularly of the rodents, yields these crystals with great facility, but their production from human blood is always an uncertain operation. A drop or so of the deeply colored liquid from a portion of clot a day or two old, may be squeezed on to a glass slide and diluted with less than its own bulk of proof spirit. Upon covering the whole loosely with a piece of microscopic glass, and setting it aside in a light but not too warm situation, flattened, prismatic, red-colored crystals will sometimes make their appearance in the course of a few hours.

(176.) Blood Stains.

These occasionally form important objects of medico-legal inquiry. The chemical evidence has

reference to the coloring matter of the blood; the microscopical to the form of the globules, and the production of hæmine crystals. Recent blood stains are of a bright red color; older stains of a reddish-brown; when on linen or other stuffs, the fibre becomes more or less stiffened.

α. **Reactions of color.** Supposing the stain to be on some stuff, a strip of the stained portion is cut off, and suspended by means of a thread in a test tube containing a little distilled water. Gradually, streaks of coloring matter will be seen descending from the stuff to the bottom of the tube, and there forming a layer, of a deep-red if the stain be recent, or a reddish-brown color if the stain be of an older date. If necessary, several of the stained strips may be thus successively treated in the same portion of water, until a sufficiently dark solution is obtained. Stains on knives and other articles are likewise to be treated with cold water, so as to obtain a solution of the coloring matter. To this red or reddish-brown solution a little dilute ammonia is added, whereby the color will be unaltered or simply brightened, but not changed to a green or crimson. When the solution of the coloring matter is boiled, its color is entirely destroyed, and a dirty brown precipitate produced. Every stain forming a reddish solution with cold water, which is unaffected by dilute ammonia, but has its color destroyed by ebullition, with the formation of a precipitate, is due to blood.

β. **Form of the corpuscles.** A little of the stained fibre, or, if possible, a little of the dried stain scraped away from the article under examination, is placed upon a glass slide and moistened with a solution of sugar (syrup diluted with about twice its bulk of water) or of pure glycerine reduced to the sp. gr. of 1028. After some time a red colored liquid will be obtained, which may be covered with a piece of microscopic glass, and examined by a good quarter-inch object-glass. Should the stain be due

to blood, the corpuscles, with their characteristic appearances, may in this way be readily detected. In the event of their appearing shrivelled, the addition of a drop or two of water will cause them to expand.

γ. **Hæmine crystals.** The dry dry blood stain is extracted with a little glacial acetic acid, and the resulting liquid evaporated at a very gentle heat. In the event of no crystals being thus obtained, a minute quantity of common salt may be added to the dry residue, and the moistening with glacial acetic acid and gentle evaporation repeated. In some cases the moistening with acid has to be performed a third time, before the characteristic dark-colored rhombic crystals, often arranged in stellate groups, as shown in Fig. 69, make their appearance. The formation of the crystals seems to be facilitated by moistening the residue with water and evaporating therewith, after each evaporation with acetic acid.

Fig. 69.

(177.) Serum.

α. **General characters.** The serum is a pale yellow, transparent, somewhat viscid fluid, having a specific gravity of about 1030, while that of blood averages about 1055. It has a faintly alkaline reaction, and consists of water holding in solution albumen, fat, certain ill-defined extractive matters, and the inorganic salts. When serum is evaporated to dryness in a water-bath, its aqueous portion is driven off, and a hard, nearly transparent, horny residue left behind. Water constitutes about 80 per cent. of normal blood.

β. **Separation of albumen.** For this purpose, either of the following methods may be adopted:—*a.* The serum is put into a small capsule, an equal bulk of coarsely powdered crystals of sulphate of sodium added to it, and the whole boiled until complete coagulation takes place, when, on filtering the boiling liquid, a perfectly clear and nearly colorless solution, quite free from albumen, will rapidly pass through. This method is equally applicable to serum containing any amount of coloring matter, and even to the broken-up clot itself. *b.* The serum is made neutral or *very faintly* acid with acetic acid, boiled and filtered. By this means the whole of the albumen will coagulate in flakes and remain on the filtering paper, while a clear liquid, termed the **serosity,** will pass through. The precipitate of albumen is to be washed with hot water, and dried in a water-bath; moreover, a minute amount of earthy salts may be removed from it by boiling dilute hydrochloric acid, as also a small proportion of fat by boiling alcohol.

γ. **Properties of albumen.** Albumen, as it exists in the blood and other animal fluids, is in a state of solution, but is capable of being coagulated by heat. The temperature at which coagulation takes place varies with the alkalinity of the fluid, and with the amount of albumen present. Serum of blood coagulates at the temperature of about 160° Fahr. Albumen once coagulated cannot be obtained in the form of a solution coagulable by heat. Normal blood contains on the average about 7 per cent. of dissolved albumen. Fibrin and coagulated albumen agree in the following characters: they are insoluble in water, alcohol, and ether; but are soluble in potash, from which solution they are reprecipitated by neutralization with an acid. If to the potash solution, acetic acid be added, the albumen will be at first precipitated, but subsequently redissolved in the excess of acid. Moreover, coagulated albumen and fibrin are soluble, though with difficulty, in acetic acid. Albu-

men and fibrin dissolve in boiling hydrochloric acid, forming deep purple solutions.

When albumen or fibrin is heated upon platinum foil, a minute white ash, consisting principally of phosphate of calcium, remains. This proportion of earthy phosphate appears to be an integral constituent of the albuminous principles. If dried albumen or fibrin be heated in a reduction tube, into the mouth of which there have been inserted a piece of red litmus and a piece of lead paper, the red litmus will become blue and the lead paper black, reactions indicating respectively the presence of nitrogen and sulphur.

δ. **Fat of blood.** The condition in which fat exists in the serum is not well understood. Some portion of it is precipitated with the albumen, the remainder being dissolved in the serosity. As a rule, serum is perfectly bright, and fat globules cannot be detected in it by microscopical examination; yet the fat being soluble in ether, does not appear to be saponified. In order to extract the fat, the dried residue left by the evaporation of serum upon a water-bath is pulverized, and the powder agitated for some time, with three or four times its bulk of ether; the whole is allowed to subside, and after some hours the ether poured off and evaporated to dryness on a water-bath, when a small quantity of a yellow semi-solid fat will be left. This may be treated with cold alcohol, when a crystalline fat will be dissolved and an oily fat be left unacted upon.

ε. **Extractives and salts.** The serosity consists of an aqueous solution of certain ill-defined organic compounds, known as extractives, and of the usual alkaline salts. All the organic constituents of the serum, with the exception of the albumen and fat, receive the name of extractives. If the serosity be carefully evaporated almost to dryness, very beautiful cubes of common salt crystallize out. Moreover, sulphuric and phosphoric acids can readily be de-

tected; the former by the production of a white precipitate with nitrate of barium and nitric acid; the latter by the addition of sulphate of magnesium, ammonia, and chloride of ammonium, when on stirring a white crystalline precipitate is thrown down. If the serosity be evaporated to dryness, and ignited, a white fusible ash will remain, which may be examined according to the directions for the analysis of animal ashes, and will be found to contain chlorine, carbonic, phosphoric, and sulphuric acids, with potassium, and traces of calcium.

ζ. **Serum containing urea.** It is probable that the blood always contains minute traces of urea; while in certain forms of disease, particularly in Bright's disease, its amount becomes very sensible. In order to detect it, the albumen is removed from the serum by either of the methods described in par. β, and the serosity evaporated carefully to dryness. If the process *b* be adopted, and the chloride of sodium in the dried residue be seen to crystallize in well-marked octahedrons instead of cubes, the presence of urea is tolerably certain. In any case the dry residue is warmed with a little strong alcohol and filtered, the alcoholic filtrate evaporated to dryness, the residue dissolved in a very small quantity of distilled water, and the aqueous solution filtered and concentrated in a watch-glass. To the cold concentrated liquid, an equal bulk of cold colorless nitric acid is next added, when, if urea be present, a crystalline deposit of nitrate of urea will be produced, which can be examined microscopically. The production of a crystalline deposit on the addition of nitric acid is in itself almost conclusive as to the presence of urea.

η. **Serum containing bile.** In jaundice, the serum of the blood is of a much darker yellow color than usual, owing to the presence of biliary coloring matter, which may be identified by adding to the serum a little nitric acid, when the albumen will be precipitated of a bluish or greenish color: or some of

the serum, just neutralized with acetic acid, may be precipitated with excess of alcohol, the alcoholic solution evaporated to a small bulk in a water-bath, and residue examined by Pettenkofer's test, and by the nitric acid test (par. 153 β).

θ. **Serum containing sugar.** Sugar exists abundantly in the blood, in cases of diabetes. Recent researches have moreover shown that the *post-mortem* blood of the inferior cava, and of the right side of the heart, habitually contains sugar in very definite amount. In order to detect it, the albumen of the blood must be removed by means of sulphate of sodium, as in par. 177 β, and to the clear filtrate a drop or two of a solution of sulphate of copper, and then an excess of caustic potash be added, whereby a deep blue-colored liquid will be produced, which, on the application of heat, will deposit a red or orange-yellow colored precipitate of suboxide of copper. The alkaline solution of tartrate of copper described in par. 162 δ may be conveniently substituted for the mixture of sulphate of copper and caustic potash.

§ VIII.—MISCELLANEOUS ANIMAL PRODUCTS.

(178.) Bile.

α. **Composition.** Human bile contains the sodium salt of a peculiar acid known as glycocholic acid, having a similar constitution to the glycobenzoic or hippuric acid found in urine. It also contains in small quantity the sodium salt of taurocholic acid. These glycocholates and taurocholates, when boiled with dilute hydrochloric acid, absorb water, and break up into cholic acid and glycocine and taurine respectively, thus :—

Glycocholic, $C_{26}H_{43}NO_6 + H_2O = C_{24}H_{40}O_5 + C_2H_5NO_2$

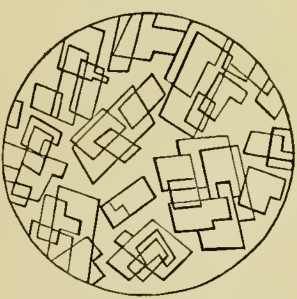
Taurocholic, $C_{26}H_{45}NO_2S + H_2O = C_{24}H_{40}O_5 + C_2H_7NO_3S$

The bile also contains water, mucus, cholesterine, fat and coloring matter, the reactions of which last have been described under the head of biliary urine (par. 153).

β. **Detection of cholic acid.** This is effected by Pettenkofer's test, which is performed in the following manner: To a little diluted bile, or any liquid containing bile, rather more than half its bulk of strong sulphuric acid is added very gradually, the tube in which the mixture is made being kept cool by immersion in water. A minute quantity of powdered white sugar, or its equivalent of syrup, is then introduced, the liquid well agitated and mixed with more sulphuric acid. By this means the temperature is gradually raised to the requisite point, when a deep purplish-crimson color makes its appearance. Very minute quantities of bile may be detected by evaporating any suspected liquid with a drop of sulphuric acid and a decigrain of sugar in a water-bath.

γ. **Biliary calculi.** Concretions of variable appearance are occasionally formed in the gall-bladder, sometimes in very considerable numbers. When numerous, they are of about the size of peas, and have an irregular angular shape, with flattened sides. When solitary, they are usually of larger bulk and of an oval form. They have a soapy feel, a fawn-yellow color, and are easily crushed by pressure. They consist principally of *cholesterine* and an insoluble combination of *bile pigment with lime.* When rich in cholesterine, they float upon water. To detect cholesterine, the powdered calculus is boiled in alcohol, and the solution filtered, when, on

Fig. 70.

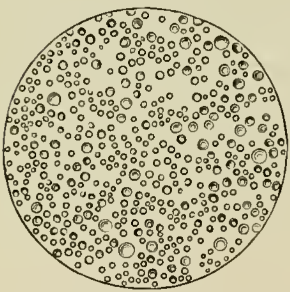


cooling, colorless transparent plates crystallize out of the yellow liquid. These crystals, when examined microscopically, are seen to consist of delicate, nearly square, rhombic plates, superimposed one upon the other as shown in Fig. 70. Cholesterine $C_{26}H_{44}O$, is soluble in ether and hot alcohol, very slightly soluble in cold alcohol, not at all soluble in water. It seems to be a species of solid alcohol.

(179.) MILK.

This secretion consists of water holding in solution **casein, lactine,** and **salts,** and holding in suspension an abundance of **fat globules,** to the presence of which the opaque white appearance of milk is due. Normal milk has an alkaline reaction to test paper. The specific gravity of human milk averages about 1030.

Fig. 71.



α. **Fat globules.** These may be easily recognized under the microscope—they are of various sizes, and have well-defined dark margins, as shown in Fig. 71. They appear to be surrounded by delicate cell-membranes, as they cannot be made to unite by pressure until after the addition of a little acetic acid. The milk secreted soon after delivery contains large, granular, fatty corpuscles, known as colostrum corpuscles. In milk abscess, &c., pus and blood globules may be occasionally detected.

β. **Casein.** When ordinary or skimmed milk is evaporated, a scum forms on its surface, which, if removed, is soon replaced by a fresh one, and so on repeatedly. This property of forming a scum on

evaporation was formerly considered peculiar to fluids containing casein. Casein differs from the other albuminous bodies in being coagulable not by heat, but by the addition of a little very dilute acid, or by contact with decomposing animal membrane. Cheese is casein which has been precipitated by rennet, the dried decomposing lining membrane of the stomach of the calf. When skimmed milk is rendered slightly acid with acetic acid, and gently warmed, the casein coagulates, and may be collected on a filter, washed with hot water, and subsequently with hot alcohol: it manifests all the usual properties of the albuminous bodies.

γ. **Lactine.** Sugar of milk, or lactine, may be readily detected in whey which has been separated by filtration from the coagulated casin. On adding a drop or two of sulphate of copper, and then an excess of potash, a red precipitate of suboxide of copper will be produced on boiling the mixture. Sugar of milk may be obtained crystalline by careful evaporation of the whey. It does not readily undergo the alcoholic fermentation; but by the action of putrefying curd becomes rapidly converted into lactic acid.

δ. **Mineral salts.** The ash of milk contains the same constituents as most animal ashes; the relative proportion of earthy phosphates is very large, and potassium exists in it to a greater extent than sodium.

(180.) Bone.

Bone consists principally of phosphate of calcium, deposited in an animal basis. When bone is soaked for some time in dilute hydrochloric acid, its earthy matter is dissolved out, and a flexible elastic mass, having the exact form of the original bone, is left unacted upon. This residue consists of gelatine, which by long boiling dissolves in water, forming a solution that gelatinizes on cooling. The solution is precipitated by tannic acid, but not by acetic acid

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or by ferrocyanide of potassium. Pure gelatine does not contain sulphur. By the incineration of bone, its animal matter is burnt off, and a brittle, white, earthy residue, having the exact form of the original bone, remains. This earthy residue consists principally of phosphate of calcium, with a little carbonate of calcium and phosphate of magnesium, also minute quantities of fluoride of calcium; which latter substance may be detected more readily, however, in fossil bones.

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